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Journal of the Mineralogical Society of America

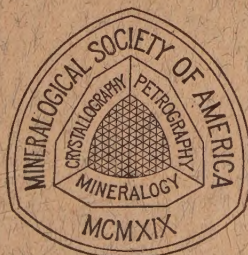
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SEPTEMBER-OCTOBER, 1953

Nos. 9 and 10

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Nos. 9 and 10

SAHAMALITE, A NEW RARE EARTH CARBONATE MINERAL¹

HOWARD W. JAFFE, ROBERT MEYROWITZ AND HOWARD T. EVANS, JR.,
U. S. Geological Survey, Washington, D. C.

ABSTRACT

Sahamalite, $(\text{Mg, Fe})(\text{Ce, La, Nd, Pr})_2(\text{CO}_3)_4$, a new rare earth mineral, occurs in barite-dolomite rock near Mountain Pass, San Bernardino County, California. The mineral is monoclinic, $2/m$; space group $P 2_1/a$; $a:b:c = 0.3635:1:0.2857$; $a_0 = 5.92 \text{ \AA}$, $b_0 = 16.21 \text{ \AA}$, $c_0 = 4.63 \text{ \AA}$, $\beta = 106^\circ 45'$. Crystals are tabular, parallel to $\{201\}$; dominant forms are $\{201\}$, $\{\bar{1}31\}$, $\{120\}$, $\{110\}$, $\{010\}$, and $\{011\}$. Cleavage (010) is poor; $\alpha = 1.679$, $\beta = 1.776$, $\gamma = 1.807$; biaxial negative, $2V = 57^\circ$; $Z \wedge c = 29^\circ$, $Y = b$; $G = 4.30$. The mineral is named for Th. G. Sahama, contemporary Finnish geochemist.

INTRODUCTION

In the summer of 1951 the senior author was assigned to make a detailed study of the mineralogy of the bastnaesite-bearing deposits near Mountain Pass, San Bernardino County, California. At this time, several rock specimens previously collected by D. F. Hewett, J. C. Olson, and W. N. Sharp, all of the U. S. Geological Survey, were made available for preliminary study. One thin section of dolomite, collected from the Sulfide Queen deposit, contained numerous small (0.01–0.2 mm.) prisms of an unidentified colorless mineral intimately associated with parisite and altered bastnaesite. After examination of the powdered mineral by the immersion method revealed unique optical properties, the mineral was purified for further studies. Subsequent spectrographic, x-ray, and chemical analyses have established the mineral to be a new anhydrous carbonate of the cerium earths, magnesium, and iron. The composition of the new mineral is expressed by the formula $\text{AB}_2(\text{CO}_3)_4$, where A is magnesium and bivalent iron and B is the cerium earth group—dominantly cerium, lanthanum, and neodymium.

The new mineral, sahamalite (sä'hä-mä-lit), is named for Thure Georg Sahama, contemporary Finnish geochemist, who has contributed much to our knowledge of the association and the abundance of the rare earths in eruptive rocks and in minerals.

¹ Publication authorized by the Director, U. S. Geological Survey.

MINERALOGY

Separation and purification

The sahamalite was difficult to separate and purify because of its fine grain size and intimate association with parisite and bastnaesite. The rock containing it was ground to minus 40 mesh, and the powder was then further sized on 60, 100, 200, and 270 mesh sieves. Microscopic studies of the different fractions showed that the sahamalite grains could not be liberated for concentration in sizes coarser than 100 mesh. The optimum concentration of the mineral amenable to separation occurred in the 100–200 mesh fraction (0.075–0.15 mm.). Sahamalite finer than 270 mesh could not be separated successfully.

Heavy-liquid separation of the sized sample was made using methylene iodide having a density of 3.3. This separation gave a light fraction composed essentially of dolomite and a minor amount of quartz, and a heavy fraction composed of barite, sahamalite, altered bastnaesite, parisite, and hematite. Barite, the chief mineral component of the heavy fraction, was removed on the Franz isodynamic magnetic separator. The barite remained nonmagnetic at the highest intensity, 1.5 amperes, and was easy to remove after several passes. Sahamalite was found to be slightly more magnetic than bastnaesite and parisite, and slightly less magnetic than hematite. Both separations had to be made at differences of only 0.1 ampere. About 50 passes on the magnetic separator were necessary to remove the altered bastnaesite, parisite, and hematite from the sahamalite. The final magnetic concentrate of sahamalite was examined microscopically and still showed a minor amount of small adhering particles of dolomite and a little red stain on some of the sahamalite grains. These impurities were removed by treating the concentrate with tartaric acid after solubility tests were made. Sahamalite is insoluble in boiling tartaric acid, whereas dolomite is completely soluble, (see solubility). Examination of the concentrate before and after the tartaric acid treatment was made by x-ray diffraction and immersion studies. The x-ray spacings and optical properties remained precisely the same. A final product of 200 mg. of sahamalite was obtained for further studies. A microscopic grain count of the final concentrate indicated 99 per cent purity.

Space group and unit cell

A single (100–200 mesh) grain of sahamalite, with the aid of its external crystal habit, was mounted on a glass fiber with the monoclinic *b*-axis oriented roughly normal to the fiber. From this crystal, photographs of the zero layer reciprocal lattice planes normal to (110) and (010), and a first layer normal to (010), were made with the Buerger

TABLE 1. X-RAY CRYSTALLOGRAPHY OF SAHAMALITE

Crystal class: Monoclinic, $2/m$
Space group: $P2_{1/a} = C_2^5h$
Lattice dimensions: $a = 5.92 \pm .02 \text{ \AA}$
 $b = 16.21 \pm .05 \text{ \AA}$ $\beta = 106^\circ 45'$
 $c = 4.63 \pm .02 \text{ \AA}$ Cell volume = $425.6 \text{ \AA}^3$
Cell contents: 2 formulas of $(\text{Mg,Fe})\text{Ce}_2(\text{CO}_3)_4$
Density: pycnometer = 4.30
calculated = 4.30 (Mg:Fe = 85:15)

precession camera using Mo/ $K\alpha$ radiation. The x-ray crystallographic data obtained by Howard T. Evans are given in Table 1.

X-ray powder diffraction pattern

An x-ray powder diffraction pattern was taken by F. A. Hildebrand with a Debye-Scherrer camera (114.59 mm. diameter) using Cr $K\alpha$ radiation with $\lambda = 2.2909 \text{ \AA}$. All the lines measured, down to $d = 1.81$, were indexed on the basis of the data given in Table 1. The x-ray powder diffraction data are given in Table 2. The pattern is reproduced in Fig. 1.

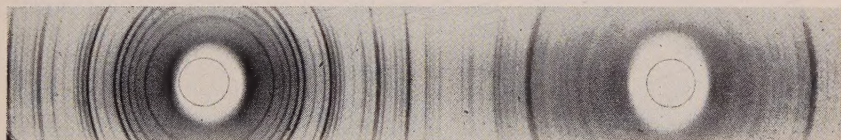


FIG. 1. X-ray powder diffraction pattern of sahamalite taken with a 114.59 mm. diameter camera using Cr $K\alpha$ radiation.

Morphology

Three grains not larger than 0.2 mm. were mounted on glass fibers and studied with the optical goniometer. The crystals were found to be rather richly developed, each showing 11 to 24 measurable faces giving fair to good signals. The data were plotted on a gnomonic projection normal to (010) and the various forms identified by comparison with the x-ray lattice. The morphological data obtained by Howard T. Evans are summarized in Table 3.

Fifteen forms were identified. The crystals are tabular parallel to $\sigma\{\bar{2}01\}$, which is by far the most prominent form. The edges are beveled by the forms $e\{120\}$ and $s\{\bar{1}31\}$. These together with other minor forms result in the characteristic habit shown in Fig. 2. Under the microscope, the crystals lie habitually on the large $\sigma(\bar{2}01)$ face and present the characteristic appearance shown in Fig. 3. The peculiarly tapering outlines of the bevel faces at the edges of the crystal are thus readily explained. The

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR SAHAMALITE

<i>d</i> (obs.)	<i>I</i>	<i>d</i> (calc.)	<i>hkl</i>	<i>d</i> (obs.)	<i>I</i>	<i>d</i> (calc.)	<i>hkl</i>
8.0	4	8.105	020	2.02	2	2.026	080
5.33	7	5.352	110			2.018	171
4.64	5	4.646	120			2.002	142
4.41	2	4.436	001			1.995	222
4.26	7	4.278	011	1.98	2	1.979	231
4.02	4	4.052	040			1.956	260
		3.990	111			1.945	042
3.90	10	3.912	130	1.94	3	1.941	261
		3.891	021			1.940	311
3.65	10	3.670	121	1.93	2	1.923	232
3.41	$\frac{1}{2}$	3.428	031			1.908	180
3.28	5	3.297	140	1.90	2	1.899	321
		3.274	131	1.88	3	1.883	241
3.03	7	3.034	111			1.877	152
2.98	1	2.992	041			1.876	112
2.87	10	2.888	141			1.853	171
		2.886	121	1.84	2	1.843	081
2.82	2	2.835	200			1.842	122
		2.814	150			1.841	320
		2.793	210			1.837	331
2.78	4	2.780	201			1.835	242
2.76	4	2.740	211	1.83	6	1.830	052
2.69	4	2.702	060	1.82	6	1.818	181
		2.681	131	1.81	2		
2.67	4	2.676	220	1.784	2		
		2.629	221	1.748	$\frac{1}{2}$		
2.60	4	2.617	051	1.707	5		
		2.547	151	1.688	3B		
		2.510	230	1.663	3B		
		2.472	231	1.629	4B		
2.45	2	2.456	141	1.610	2		
2.42	3	2.439	160	1.595	1		
2.32	3	2.323	240	1.573	2		
2.28B	6	2.292	241	1.534	2		
		2.280	112	1.514	4		
2.25	1	2.259	161	1.486	3		
		2.253	151	1.475	4		
2.21	2	2.218	002	1.437B	2		
		2.215	122	1.393	5		
2.19	2	2.197	012	1.378	5		
		2.144	170	1.361	1		
		2.140	022	1.353	1		
		2.134	250	1.332B	3		
2.12B	7	2.127	201	1.317B	1		
		2.118	132	1.302	4		
2.10B	7	2.110	251	1.295B	5		
		2.109	211	1.267B	2		
2.05B	6	2.058	202	1.244B	1		
		2.057	221	1.233B	2		
		2.053	071	1.222B	2		
		2.052	032	1.2048B	2		
		2.042	212	1.1914B	1		
		2.033	161	1.1845B	1		

B = broad.

TABLE 3. MORPHOLOGICAL CRYSTALLOGRAPHY OF SAHAMALITE

Crystal class: Monoclinic, $2/m$ *Elements (from Table 1)*Axial ratio $a:b:c=0.3635:1:0.2857$, $\beta=106^{\circ}45'$ Projection: $x_0'=0.3010$; $p_0'=0.8169$; $q_0'=0.2857$ Polar: $p_0=0.7162$; $q_0=0.2505$; $\nu_0=73^{\circ}15'$ *Forms observed:*

b 010	f 011	q $\bar{1}11$	s $\bar{1}31$
e 120	d 021	γ $\bar{1}42$	n $\bar{2}11$
m 110	σ $\bar{2}01$	G $\bar{3}23$	x $\bar{2}51$
l 230	k $\bar{1}12$	a 343	

Dominant forms (descending rank):

 σ, s, e, m, b, f

upper and lower corners of the crystal are usually truncated at a shallower angle by the form $m\{110\}$ which is generally striated in oscillatory growth with $e\{120\}$. It may be noted that two of the three measured crystals gave projections corresponding to the normal habit, but the third showed a number of poorer reflections grouped around the principal forms. These poorer reflections appear to correspond to vicinal forms produced by etching and partial solution of some of the faces.

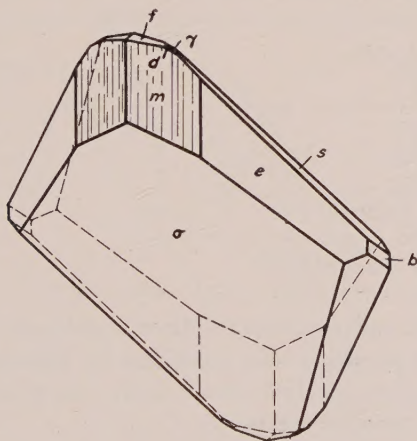
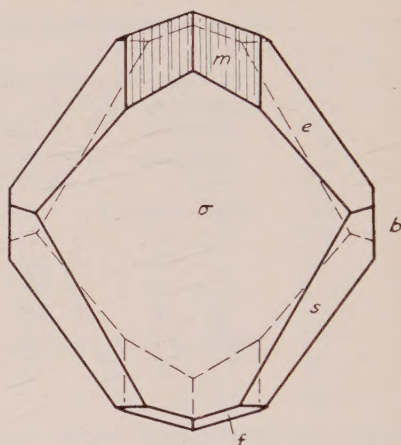
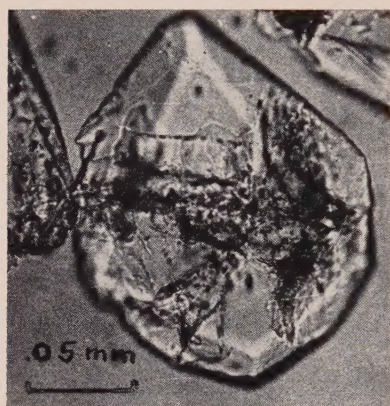


FIG. 2. Typical crystal habit of sahamalite showing forms $\sigma(\bar{2}01)$, $m(110)$, $e(120)$, $b(010)$, $s(\bar{1}31)$, $f(011)$, $d(021)$, and $\gamma(\bar{1}42)$.

Optical properties

Sahamalite is colorless and nonpleochroic in thin section and in fragment mounts. Grains lying on the prominent $(\bar{2}01)$ face give a birefringence of 0.028; those lying on (010) give the maximum birefringence of 0.128. Cleavage is poor parallel to (010) , and traces may be observed

FIG. 3. Appearance of crystal of sahamalite resting on $\sigma(\bar{2}01)$ face.

occasionally on grains lying on $(\bar{2}01)$. The optical constants measured by H. W. Jaffe are given in Table 4, and the optic orientation is illustrated in Fig. 4.

TABLE 4. OPTICAL PROPERTIES OF SAHAMALITE

Index of refraction (± 0.002)	Orientation
$\alpha = 1.679$	$X \wedge a$
$\beta = 1.776$	$Y = b$
$\gamma = 1.807$	$Z \wedge c = 29^\circ$
$2V$: (Universal stage) $= 57^\circ(-)$	
(Calculated) $= 57^\circ(-)$	
Dispersion: $r < v$ (perceptible)	

The intermediate and maximum indices of refraction were measured with the index oils prepared and described by Meyrowitz and Larsen (1951). Index oils were checked with a Leitz-Jelley microrefractometer at the time the indices were measured.

CHEMISTRY

Solubility

In the course of the separation and chemical analysis of sahamalite, some data were obtained on its solubility. The mineral is more resistant to acids than most normal carbonates. This is illustrated in Table 5, where sahamalite is compared with the National Bureau of Standards sample #88 dolomite.

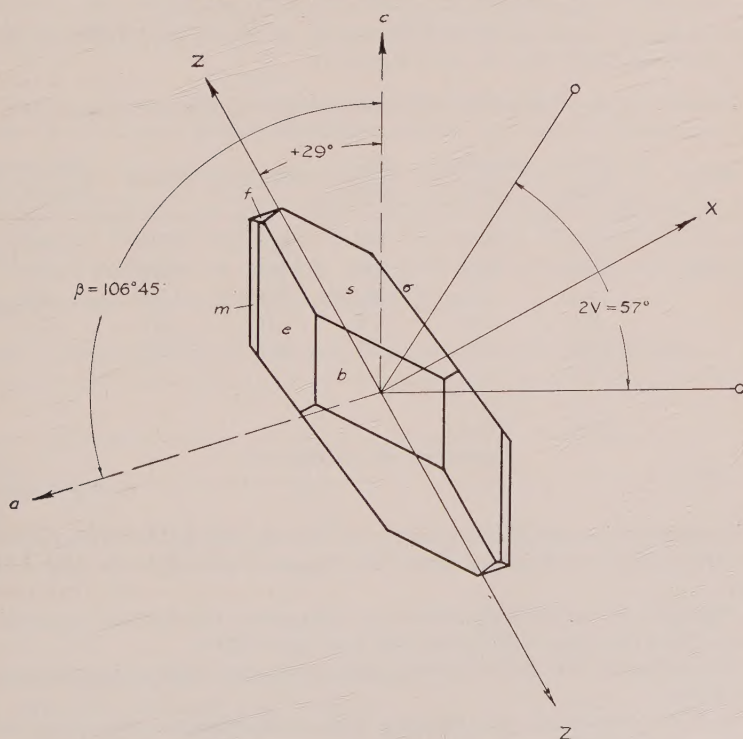
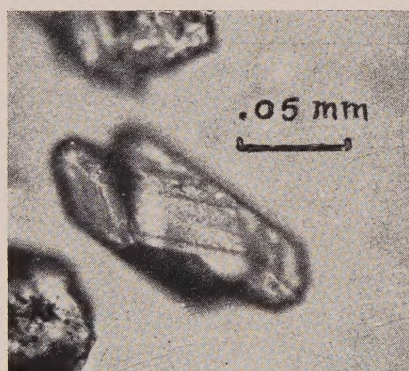


FIG. 4. Optical orientation of sahamalite.

TABLE 5. RELATIVE SOLUBILITIES OF SAHAMALITE AND DOLOMITE

Acid	Dolomite	Sahamalite
Boiling tartaric	soluble	insoluble
Boiling 1N HCl	soluble	insoluble
Boiling 3N HCl	soluble	soluble

TABLE 6. SPECTROGRAPHIC ANALYSIS OF SAHAMALITE

X0.	La, Ce
X.	Mg, Fe, Nd
.X	Mn, Ba, Si
.0X	Pb, Al, Ca, Y
.00X	Cu, Sr
.000X	Ag, Be

Looked for, not found: Au, Pt, Mo, W, Ge, Sn, As, Sb, Bi, Zn, Cd, Tl, Co, Ni, Ga, Cr, V, Yb, Ti, Zr, Th, U, Nb, Ta, B, F, K, and Na.

TABLE 7. CHEMICAL ANALYSIS OF SAHAMALITE (ROBERT MEYROWITZ, *analyst*)

Oxide	Deter- mined	Recalcu- lated	Mol. ratios	Oxygens	Metals	Cations on basis of 12 O
Ce ₂ O ₃	31.4	31.7	966	2898	1932	1.06
(La, Nd) ₂ O ₃	27.8	28.1	848	2544	1696	.93
MgO	6.1	6.2	1538	1538	1538	.85
FeO	2.0	2.0	278	278	278	.15
CO ₂	31.7	32.0	7271	14542	7271	4.00
Insol.	0.5	—				
	99.5	100.0				
		Density = 4.30 (pycnometer)				

Notes:

1. Cerium was determined volumetrically by titrating with 0.01N ferrous ammonium sulfate after oxidation with sodium bismuthate. The size of the sample was approximately 10 mg.

2. The figure for the rare-earth oxides other than cerium was obtained by subtracting the sum of the percentages of Fe₂O₃ and CeO₂ from that of R₂O₃.

3. Magnesium was determined as the pyrophosphate. Size of the sample was approximately 23 mg.

4. Iron was determined colorimetrically with o-phenanthroline. Size of the sample was approximately 2 mg.

5. CO₂ was obtained by loss on ignition, using a sample of approximately 8 mg. A CO₂ determination by the macroabsorption train method gave 30 per cent.

6. No H₂O was found by the Penfield method.

7. Rare earths other than cerium were determined by quantitative spectrochemical analysis, H. J. Rose, Jr., analyst. La₂O₃ 17.4, Nd₂O₃ 7.3, Pr₂O₃ 2.3, Sm₂O₃ 0.7; total 27.7. Rare earth ratio is Ce:La:Nd:Pr:Sm = 53:30:12:4:1.

Composition

Prior to quantitative chemical analysis, the sample was submitted for semiquantitative spectrographic analysis. The spectrogram obtained by H. J. Rose, Jr., gave the percentages shown in Table 6. The complete chemical analysis of sahamalite is given in Table 7.

The formula derived from the chemical analysis given in Table 7 is written as follows: $(\text{Mg, Fe}) (\text{Ce, La, Nd})_2(\text{CO}_3)_4$ or $\text{AB}_2(\text{XO}_3)_4$

where A Mg^{+2} Fe^{+2}

B Ce^{+3} , La^{+3} , Nd^{+3}

X C^{+4}

Sahamalite is not related to any of the known carbonate mineral groups or miscellaneous types listed in the *Dana's System of Mineralogy* (Palache et al., 1951). No naturally occurring anhydrous normal carbonates of the $\text{AB}_2(\text{XO}_3)_4$ type are known. Using the Dana System classification, sahamalite might be categorized as follows:

Carbonates

Class 14. Anhydrous normal carbonates

Type 4. $\text{AB}_2(\text{XO}_3)_4$.

The presence of essential magnesium and bivalent iron in A and the various members of the cerium earth group in B suggests that appreciable substitution may be expected in the sahamalite type, $\text{AB}_2(\text{XO}_3)_4$. The theoretical composition for Mg and Fe^{+2} end members are compared with the composition of sahamalite in Table 8.

TABLE 8. COMPOSITION OF SAHAMALITE AND Mg , Fe^{+2} END MEMBERS

	1	2	3
Ce_2O_3	30.2	31.7	28.6
$(\text{La, Nd, Pr})_2\text{O}_3$	30.0	28.1	28.3
MgO	7.4	6.2	—
FeO	—	2.0	12.5
CO_2	32.4	32.0	30.6
	100.0	100.0	100.0

1. Theoretical Mg end member, with Ce:La 1:1.
2. Sahamalite, Mountain Pass, California.
3. Theoretical Fe^{+2} end member, with Ce:La 1:1.

Relation between composition, index of refraction, and density

The application of the law of Gladstone and Dale (1864) to mineralogy, suggested by Larsen and Berman (1934), has not been sufficiently exploited by mineralogists. The simple equation $(n-1)/d = K$, where n

is the mean index of refraction, d is the density, and K is the sum of the specific refractive energies of the component oxides (k), proved very useful in establishing the composition of sahamalite during the early stages of this investigation.

The spectrographic analysis was followed by a preliminary chemical analysis to determine whether sahamalite was a normal carbonate or a fluocarbonate, and to establish the methods best suited for the analysis of the small sample available. The preliminary analysis gave:

R ₂ O ₃	59%
MgO	6
FeO	2
CO ₂	21
	—
Total	88%

After qualitative tests for fluorine and H₂O proved negative, the spectrogram was reexamined. No additional metallic constituents could be found, and a second spectrographic analysis was made with the same results. Using the indices of refraction, the pycnometer density, the analytical data, and the specific refractive energies of the oxides (k) given by Larsen and Berman (1934), it was calculated from $(n-1)^2/d = K$ that the missing oxide or element had a specific refractive energy (k) near .20. Eliminating the elements previously not detected with the spectrograph, this left only CO₂ ($k=0.217$), Br ($k=0.214$), I ($k=0.226$), and O ($k=.203$) to account for the 12 per cent missing from the analytical total. The CO₂ determination was repeated by two different methods and the correct value was obtained bringing the analytical total to 99 per cent. The original CO₂ determination was low because the macroabsorption train had recently been set up and was not in equilibrium.

Crystal chemistry

From the data now available, the coordination of the various cations in sahamalite may be predicted from Pauling's (1929) electrostatic valency principle. In sahamalite, each oxygen should be common to:

1 C ⁺⁴ in threefold coordination equal to	1 $\frac{1}{3}$
1 (Mg, Fe) ⁺² in sixfold coordination equal to	$\frac{1}{3}$
1 (Ce, La) ⁺³ in ninefold coordination equal to	$\frac{1}{3}$
	—
Total positive charge=2	

In this manner, the total strength of the valency bonds that reach an oxygen ion from all neighboring cations is equal to a positive charge of 2, satisfying Pauling's rule. Mg⁺² and Fe⁺² are normally expected to assume sixfold coordination, and C⁺⁴ would normally be in threefold coordination in minerals. Ce⁺³ and the other large trivalent rare-earth

ions would be expected to assume a coordination in the range of eight to twelve. From a consideration of Pauling's rule, Ce^{+3} should be in nine-fold coordination in sahamalite.

OCCURRENCE

Geological environment

The geology of the Mountain Pass district is described by D. F. Hewett, J. C. Olson, et al. (U. S. Geological Survey Bulletin, in preparation). Carbonate-rich rocks, composed essentially of calcite, dolomite, barite, quartz, and bastnaesite, occur as veins and irregular bodies in foliated metamorphic rocks and in alkalic igneous rocks including shonkinite, syenite, and quartz syenite. The largest of the irregular carbonate-rich bodies, locally referred to as the Sulfide Queen, contains barite and bastnaesite throughout; but thus far, sahamalite has been detected in only about one acre of area in the southwestern part of the exposed Sulfide Queen body.

Mineral association

Sahamalite occurs in a medium- to coarse-grained, light- to dark-brown barite-dolomite rock. Three modal analyses of the rock (Table 9) show a variable mineralogical composition. The Modes for samples 123 A and B were obtained from two thin sections cut from the same rock specimen.

TABLE 9. MODES OF SAHAMALITE-BEARING BARITE-DOLOMITE ROCK

	123A	123B	123C
Dolomite	46*	40*	60*
Barite	39	25	22
Sahamalite	8	13	4
Parisite } Bastnaesite }	5	20	10
Quartz	1	1	3
Hematite	1	1	1
	100	100	100

* Contains approximately 1 per cent ankerite+calcite.

The thin sections show well-developed rhombs of dolomite, 0.5 to 2.0 mm. in diameter, in a matrix of fine- to medium-grained barite. The barite is commonly strained and the dolomite rhombs commonly broken. Sahamalite characteristically occurs in subparallel, radiating clusters of singly terminated prisms, 0.01 to 0.2 mm. in size (Fig. 5). Parisite and

altered bastnaesite are intimately associated with sahamalite, and all three of the rare-earth minerals form fringes around the dolomite grains (Fig. 6). Sahamalite also embays the dolomite rhombs along cleavage traces. The accessory minerals are quartz, hematite pseudomorphous after pyrite, calcite, and ankerite. Fine- to medium-grained, granular,



FIG. 5.

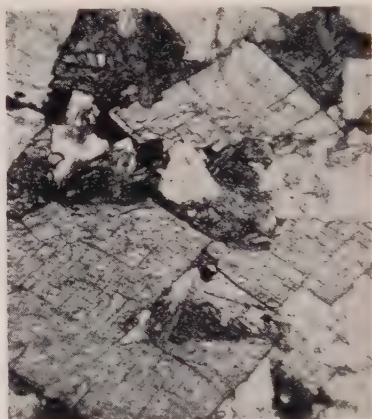


FIG. 6.

FIG. 5. Well-developed elongate crystals of sahamalite in quartz. Small, well-formed hexagon at bottom of photograph is parisite. Dirty, mottled material at top of photograph is altered bastnaesite. Center of photograph shows barite being replaced by quartz. Pl. pol. lt. $\times 100$.

FIG. 6. Rhombic grains of dolomite partly replaced by barite (gray-white), quartz (clear white), and the rare earth minerals: sahamalite, parisite, and altered bastnaesite (dark grains with high relief). Opaque grains are hematite. Pl. pol. lt. $\times 50$.

strained barite occurs in lenticular masses and veinlets replacing dolomite and frequently isolating patches of dolomite grains. Where the dolomite is badly deformed, the rhombs take on a strained plumose habit characteristic of dolomitic rocks elsewhere in the Sulfide Queen deposit. Bastnaesite is badly altered and could not be positively identified by microscopic means. Its identity was confirmed by x-ray powder diffraction analysis. The altered bastnaesite exhibits a fine-grained, dirty appearance, commonly showing a brown stain. In contrast to the bastnaesite, sahamalite and parisite form fresh, moderately well-developed prisms and plates.

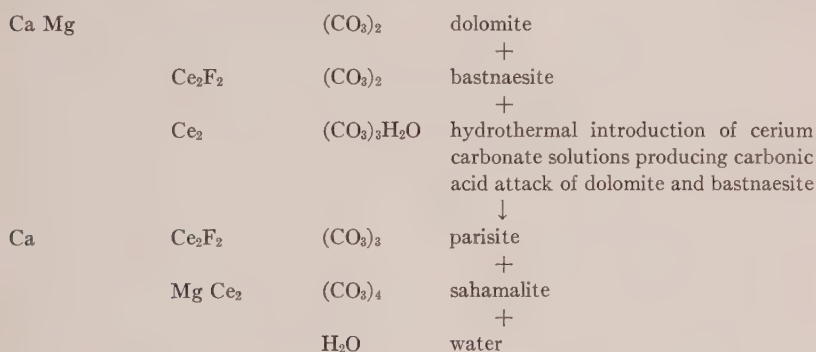
Paragensis

In thin sections *A* and *B* of specimen 123 the dolomite is interpreted to be the oldest mineral. Formation of dolomite was followed by the introduction of bastnaesite and barite. Sahamalite and parisite accom-

TABLE 10. THEORETICAL COMPOSITIONS OF DOLOMITE, BASTNAESITE, PARISITE, AND SAHAMALITE

Mineral	Ce-earth oxides	F	CaO	MgO	CO ₂
Dolomite	—	—	30.4	21.9	47.7
Bastnaesite	74.8	8.69	—	—	20.2
Parisite	60.8	7.07	10.4	—	24.6
Sahamalite	59.2	—	—	7.4	32.4

panied by quartz are believed to be the last minerals to crystallize. The order of rare-earth mineral crystallization—bastnaesite, parisite, and sahamalite—is consistent with a decreasing availability of fluorine as indicated in Table 10. Bastnaesite and parisite contain essential fluorine, whereas sahamalite has none. It is inferred that parisite and sahamalite have formed from dolomite and bastnaesite under hydrothermal conditions. The following reaction is suggested as a potential explanation for the formation of parisite and sahamalite:



All the available calcium from the dolomite would enter parisite, and all the magnesium would enter sahamalite. The data in Table 10 clearly show that the CaO:MgO ratio in theoretical dolomite is nearly equal to the CaO:MgO ratio in theoretical parisite plus sahamalite. The ratio, 30.4 CaO:21.9 MgO is virtually the same as 10.4 CaO (parisite):7.4 MgO (sahamalite). This would suggest that no calcium or magnesium need be introduced for the formation of parisite and sahamalite from dolomite and bastnaesite. The only introduction required is cerium, carbon dioxide, and water, the latter to generate carbonic acid for the alteration of dolomite and bastnaesite. If additional fluorine were added, the suggested reaction would not have occurred, and additional bastnaesite should have crystallized. Inasmuch as the rock does not contain any

fresh bastnaesite, the larger crystals of sahamalite associated with late quartz are further suggestive of local hydrothermal activity in the barite-dolomite rock.

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REFERENCES

- GLADSTONE, J. H., AND DALE, T. P. (1864), Researches on the refraction, dispersion and sensitiveness of liquids: *Roy. Soc. London Philos. Trans.*, **153**, 337.
- LARSEN, E. S., JR., AND BERMAN, H. (1934), The Microscopic Determination of the Non-opaque Minerals: *U. S. Geol. Survey, Bull.* **848**, p. 30-32.
- MEYROWITZ, R. M., AND LARSEN, E. S., JR. (1951), Immersion liquids of high refractive index: *Am. Mineral.*, **36**, 746-750.
- PALACHE, C., BERMAN, H., AND FRONDEL, C. (1951), *Dana's System of Mineralogy*, vol. 2, 7th ed., John Wiley & Sons, New York.
- PAULING, L. (1929), *Jour. Am. Chem. Soc.*, **51**, 1010.

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MANGANPYROSMALITE AND ITS POLYMORPHIC RELATION TO FRIEDELITE AND SCHALLERITE*

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ABSTRACT

Manganpyrosmalite, $(\text{Mn}, \text{Fe})_8(\text{Si}_6\text{O}_{15})(\text{OH}, \text{Cl})_{10}$, is a new species isostructural with pyrosmalite. It occurs at Sterling Hill, New Jersey, as granular veinlets in franklinite ore. Hexagonal, with a_0 13.36 Å, c_0 7.16; $Z=2$; $G=3.13$ (meas.), 3.14 (calc.). Uniaxial negative, with ω 1.669, ϵ 1.631 (Na). Hardness $4\frac{1}{2}$. Perfect cleavage (0001). Color pure brown.

Manganpyrosmalite, schallerite and frielite are polymorphs representing multiple stacking variants along [0001] of layer-structures, analogous to the micas. Cell dimensions (new data):

	a_0	c_0	Lattice type	Z
Manganpyrosmalite	13.36 Å	7.16	Hexagonal	2
Pyrosmalite	13.35	7.15		
Schallerite	13.43	14.31	Hexagonal	4
Friedelite	13.40	21.43	Rhombohedral	6

All of these species show serial variation in composition by substitution of $(\text{Mn}^2, \text{Fe}^2)$, (OH, Cl) and (Si, As^3) . Ferroschallerite is discredited; it is a variety of frielite. Zeophyllite, gyrolite, truscottite, okenite and centrallassite are not related to the minerals at hand.

MANGANPYROSMALITE

Pyrosmalite, $(\text{Fe}, \text{Mn})_8(\text{Si}_6\text{O}_{15})(\text{OH}, \text{Cl})_{10}$, is known only from the magnetite deposits of Nordmark and Dannemora, Sweden. The manganese-rich analogue of pyrosmalite recently has been found in the franklinite deposit at Sterling Hill, New Jersey. The mineral occurs in massive granular form with frielite, bementite and willemite as veinlets. Individual grains range up to about 0.3 mm. in size and show a perfect basal cleavage. The cleavage surfaces are warped, and the aggregates have a somewhat schistose structure. The specific gravity is 3.13 and the hardness is $4\frac{1}{2}$. Optically, the mineral is uniaxial negative and the indices of refraction, measured in sodium light, are ω 1.669, ϵ 1.631.

An x-ray powder pattern taken in filtered iron radiation was indexed in terms of a hexagonal cell with $a_0=13.36$, $c_0=7.16$ Å, as shown in Table 1. Gossner and Mussgnug (1931) reported a hexagonal cell with $a_0=13.44$, $c_0=7.20$ kX from an x-ray rotation study of the isostructural mineral pyrosmalite, and the values $c_0=13.35$, $c_0=7.15$ Å were obtained here from rotation photographs taken in iron radiation of pyrosmalite

* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 339.

TABLE 1. X-RAY POWDER SPACING DATA FOR MANGANPYROSMALITE
 Iron radiation, manganese filter. Indexing for hexagonal cell
 with $a_0 = 13.36 \text{ \AA}$, $c_0 = 7.16$.

<i>I</i>	<i>d</i> meas.	<i>d</i> calc.	<i>hkl</i>	<i>I</i>	<i>d</i> meas.	<i>d</i> calc.	<i>hkl</i>
3	11.60	11.57	10 $\bar{1}$ 0	1	1.768	1.769	10 $\bar{1}$ 4
10	7.16	7.16	0001	1*	1.733	1.729	11 $\bar{2}$ 4
1	6.71	6.68	11 $\bar{2}$ 0	5	1.672	1.670	44 $\bar{8}$ 0
3	6.09	6.09	10 $\bar{1}$ 1	4	1.627	1.626	30 $\bar{3}$ 4
1	5.77	5.78	20 $\bar{2}$ 0	5	1.523	1.523	40 $\bar{4}$ 4
2	4.886	4.885	11 $\bar{2}$ 1	1	1.432	1.432	0005
1	4.509	4.500	20 $\bar{2}$ 1	2	1.419	1.421	10 $\bar{1}$ 5
1	4.376	4.373	21 $\bar{3}$ 0			1.416	50 $\bar{5}$ 4
2	3.736	3.732	21 $\bar{3}$ 1	2	1.371	1.385	42 $\bar{6}$ 4
8	3.583	3.580	0002			1.390	20 $\bar{2}$ 5
4	3.419	3.421	10 $\bar{1}$ 2	2	1.342	1.342	30 $\bar{3}$ 5
3	3.338	3.340	22 $\bar{4}$ 0	2	1.285	1.283	40 $\bar{4}$ 5
2	3.035	3.028	22 $\bar{4}$ 1	1	1.266	1.262	8.2.10.0
		3.040	20 $\bar{2}$ 2	1	1.238	1.244	63 $\bar{9}$ 3
2	2.882	2.892	40 $\bar{4}$ 0	1	1.194	1.195	0006
2	2.770	2.770	21 $\bar{3}$ 2	1**	1.790		
9	2.683	2.682	40 $\bar{4}$ 1	1**	1.406		
2	2.549	2.525	41 $\bar{5}$ 0	2*	1.126	1.124	22 $\bar{4}$ 6
2	2.385	2.386	0003	1**	1.106		
1	2.334	2.337	10 $\bar{1}$ 3	2**	1.089		
7	2.251	2.250	40 $\bar{4}$ 2	2**	1.082		
		2.247	11 $\bar{2}$ 3	1**	1.063		
1*	2.102	2.095	21 $\bar{3}$ 3	1**	1.047		
4	1.843	1.840	40 $\bar{4}$ 3				

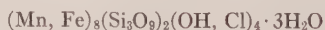
*=diffuse line; **=very diffuse line.

crystals from Nordmark. The observed x-ray unit for pyrosmalite conforms to the accepted morphological unit for this species.

A chemical analysis of the manganpyrosmalite from Sterling Hill is cited in Table 2, together with the unit cell contents calculated therefrom. Assuming the crystal structure to be based on a sheet-framework (phyllosilicate), with an Si:O ratio of 2:5, the formula may be written:



This interpretation corresponds to that taken of pyrosmalite by Berman (1937), Strunz (1949) and Winchell (1951). Two formula-units are contained in the unit cell. The specific gravity calculated from the measured cell contents is 3.14. The structure also can be assumed to be based on a three- or six-fold ring grouping for the silica framework, giving the formula:



This formula corresponds to that derived by Bauer and Berman (1928) for the composition of pyrosmalite. According to Zambonini (1908), pyrosmalite gives off only about 1.3 weight per cent H_2O below $345^\circ C$. Other formulae, differing but slightly in weight percentages, can be written depending on the way in which the O and H are arbitrarily assigned to Si, OH or H_2O (see Gossner and Mussnug (1931) and Zambonini (1901, 1908)). The phyllosilicate interpretation seems likely in view of the micaceous habit and cleavage and particularly in view of the dimensional relations to the polymorphs friedelite and schallerite described beyond.

TABLE 2. CHEMICAL ANALYSIS AND UNIT CELL CONTENTS OF MANGANPYROSMALITE

Analysis (L. H. Bauer)	Molecular quotient	Atomic quotient	Unit cell contents (Exper. M.W. = 2086)	Theory
MnO 39.09	.5511	.5511	Mn = 11.50	16
FeO 12.43	.1730	.1730	Fe = 3.61	
MgO 0.74	.0184	.0184	Mg = .38	
ZnO 1.94	.0238	.0238	Zn = .50	
CaO nil				
SiO ₂ 34.13	.5683	.5683	Si = 11.86	12
As ₂ O ₅ 0.13	.00066	.0013	As = .03	
Cl 3.80	.1072	.1072	Cl = 2.24 2.24 Cl	20
H ₂ O 8.18	.4542	.9084	H = 18.95 18.95 OH	
100.44		2.3591 (O)	O = 49.22 30.27 O for Si	30
O = Cl 0.86				
99.58				

The six reported chemical analyses of pyrosmalite, summarized by Hintze (1891), Dana (1892) and Zambonini (1901), and the present analysis of manganpyrosmalite indicate that a continuous solid solution series extends from at least Fe:Mn~1.5:1 to Fe:Mn~1:3.2. The names pyrosmalite and manganpyrosmalite are here applied to the halves of the series with Fe > Mn and Mn > Fe in atomic per cent, respectively.

RELATIONS TO OTHER MINERALS

The relations of pyrosmalite to other minerals of similar chemical, crystallographic and optical properties have been discussed by a number of investigators. Among these studies, Berman in his 1937 paper on the classification of the silicates placed pyrosmalite in a group with schallerite, friedelite, ferroschallerite and the calcium-bearing silicates zeophyllite, truscottite, gyrolite and centrallassite. All were interpreted as

TABLE 3. SPECIMENS EXAMINED BY X-RAYS IN THE PRESENT STUDY

Friedelite Pattern

Friedelite. Franklin, N. J. No. 87123. Material analyzed by Schaller, cited by Palache (1910), and cited by Bauer and Berman (1928). The original discovery specimen of friedelite at Franklin.

Friedelite. Franklin, N. J. No. 89854. Sharply developed hcmimorphic crystals comprising the material described by Palache (1935) and shown in Fig. 133 and Plate 14, Fig. C in his publication. The massive friedelite lining the specimen was analyzed by Gage, cited by Bauer and Berman (1928).

Friedelite. Franklin, N. J. No. 89432. The material analyzed by Bauer and cited by Bauer and Berman (1928). A vein of pale reddish brown material.

Friedelite. Sterling Hill, N. J. No. 89865. A low-chlorine type analyzed by L. H. Bauer in 1927 (unpublished).

Friedelite. Sterling Hill, N. J. No. 89868. Dense, dark flesh-colored vein. A partial analysis made in 1927 by L. H. Bauer, hitherto unpublished, gave Cl 2.96, As_2O_3 0.11, H_2O 9.91 $\omega=1.648$.

Friedelite. Franklin, N. J. No. 90351. Bright flesh-pink vein material.

Friedelite. Franklin, N. J. No. 89859. Brown type with massive green willemite.

Friedelite. Franklin, N. J. No. 92249.

Friedelite. Franklin, N. J. No. 90341. Dark red-brown dense material resembling serpentine.

Friedelite. Franklin, N. J. No. 91190. Crust of platy reddish brown crystals.

Friedelite. Adervielle, Hautes Pyrénées, France. No. 85643. Dense pink material.

Friedelite. Pajsberg, Sweden. No. 87122. Crystals in cavities of a magnetite-amphibole rock.

Ferroschallerite. Franklin, N. J. No. 89999. Type analyzed material of Bauer and Berman (1930). Coarse cleavable grains associated with a zinc- and manganese-bearing cummingtonite described by the same authors.

Ferroschallerite. Franklin, N. J. No. 92791. Three additional specimens which, with the foregoing, represent the three types of occurrence described by Palache (1935).

Schallerite Pattern

Schallerite. Franklin, N. J. No. 87106. The type analyzed material of Gage, Larsen and Vassar (1925), later re-analyzed by Bauer and Berman (1928). Termed by Bauer and Berman (1928) and by Palache (1935) as schallerite Type I.

Schallerite. Franklin, N. J. No. 89866. The material analyzed by Bauer and Berman (1928) and termed by them and by Palache (1935) as schallerite Type II.

Schallerite. Franklin, N. J. No. 101106. Dense reddish brown type associated with bementite. An unpublished analysis of this material made in 1950 by Mrs. Marie L. Lindberg of the U. S. Geological Survey shows it to be close in composition to the original schallerite (Type I) of Gage, Larsen and Vassar (1925).

Schallerite. Franklin, N. J. No. 90000. Dense vein. Not analyzed.

Pyrosmalite Pattern

Pyrosmalite. Nordmark, Sweden. No. 85651. Blackish brown crystals on magnetite.

Pyrosmalite. Nordmark, Sweden. No. 85650. Pale brown translucent crystals with calcite and fibrous green amphibole.

Pyrosmalite. Dannemora, Sweden. No. 96422. Brown, foliated vein-mass in magnetite-pyroxene rock. Duplicate specimen from Riksmuseets Mineralogiska Avdelning, Stockholm.

Manganpyrosmalite. Sterling Hill, N. J. No. 104001. Material described in the present study.

sheet structures. It was suggested by Berman that solid solution series involving (Fe, Mn), (OH, Cl) and (Si, As³) probably extended between friedelite, schallerite and pyrosmalite. All three species were referred to the same formula-type, the names friedelite and pyrosmalite being applied to material high in Mn and Fe, respectively, and the name schallerite to material containing much As³ in substitution for Si. Strunz (1949) has accepted the formula and the grouping advanced by Berman (1937), but has put the calcium-bearing species into a separate group. He remarks that the minerals of the Friedelite Group probably are homotypes, and points out a dimensional relationship to mica. Winchell (1951) treats pyrosmalite and friedelite as a solid solution series, the names being applied to the Fe and Mn ends of the series, respectively. Schallerite and ferroschallerite are classed separately, as are the calcium-bearing species.

NEW DATA

The mutual relations of the minerals mentioned above have been investigated here by *x*-ray single-crystal and powder methods. The study material, which included a number of analyzed specimens, is described in Table 3. The results of this work may be briefly summed as follows. Pyrosmalite and manganpyrosmalite give identical *x*-ray powder patterns and unit cell dimensions and constitute an isostructural series. Friedelite has a different and distinctive *x*-ray pattern and unit cell, and so does schallerite. The dimensional relations between these minerals prove to be of special interest. The value of a_0 of the unit cell in hexagonal coordinates for all these species is virtually identical, and the values of c_0 are almost exact multiples, as shown in Table 4. The *x*-ray powder data are tabulated in Tables 1 and 5. Manganpyrosmalite, friedelite and schallerite are polymorphs, and represent stacking variants along [0001] of layer structures analogous to the polymorphs found, for example, in the mica group.

It may be noted that type ferroschallerite is found by *x*-ray study to have the pattern and cell dimensions of friedelite. This mineral is only a

TABLE 4. UNIT CELL DIMENSIONS

	a_0	c_0	Lattice type	Unit cell contents
Pyrosmalite	13.35 Å	7.15	Hexagonal	2 (Fe, Mn) ₈ (Si ₆ O ₁₅)(OH, Cl) ₁₀
Mangan- pyrosmalite	13.36	7.16		2 (Mn, Fe) ₈ (Si ₆ O ₁₅)(OH, Cl) ₁₀
Schallerite	13.43	14.31 (=2)	Hexagonal	4 (Mn, Fe) ₈ (Si ₆ O ₁₅)(OH, Cl) ₁₀
Friedelite	13.40	21.43 (=3)	Rhombohedral	6 (Mn, $\frac{1}{3}$ Fe) ₈ (Si ₆ O ₁₅)(OH, Cl) ₁₀

TABLE 5. X-RAY POWDER SPACING DATA FOR FRIEDELITE AND SCHALLERITE
Iron radiation, manganese filter, in Å

Friedelite				Schallerite			
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
1	11.4	1	1.449	9	7.37	2	2.109
9	7.17	1	1.439	10	3.59	5	2.037
7	3.60	2	1.402	2	3.45	3	1.842
6	2.88	1	1.374	1	3.30	2	1.727
10	2.56	3	1.359	1	3.11	9	1.674
3	2.408	1	1.313	5	2.848	3	1.631
4	2.115	2	1.204	7	2.687	4	1.521
2	1.974	1	1.200	3	2.546	1	1.422
3	1.731	1	1.167	6	2.478	3	1.394
6	1.676	1	1.093	1	2.395	2	1.373
2	1.632	1	1.090	1	2.321	1	1.294
1	1.625	1	1.065	3	2.253	1	1.286
1	1.520			1	2.208	2	1.185

variety of friedelite relatively high in Fe and As, and it is not a variety of schallerite or a separate species as originally described by Bauer and Berman (1930). The name should be abandoned. X-ray powder study of centrallasite, truscottite, okenite, gyrolite and zeophyllite indicates that these minerals are not related to friedelite, schallerite or pyrosmalite-manganpyrosmalite.

REFERENCES

- BAUER, L. H., AND BERMAN, H.: *Am. Mineral.*, **13**, 341 (1928).
 BAUER, L. H., AND BERMAN, H.: *Am. Mineral.*, **15**, 340 (1930).
 BERMAN, H.: *Am. Mineral.*, **22**, 342 (1937).
 DANA, E. S.: *System of Mineralogy*, 6th ed., 465 (1892).
 GOSSNER, B., AND MUSSGUG, F.: *Zeit. Krist.*, **76**, 525 (1931).
 HINTZE, C.: *Handbuch der Mineralogie*, **2**, 519 (1891).
 STRUNZ, H.: *Mineralogische Tabellen*, 222 (1949).
 WINCHELL, A. N.: *Elements of Optical Mineralogy*, Pt. II, 4th ed., 359 (1951).
 ZAMBONINI, F.: *Zeit. Krist.*, **34**, 554 (1901).
 ZAMBONINI, F.: *Atti Acc. Sc. Napoli*, **16**, no. 1 (1908); *Zeit. Krist.*, **49**, 79 (1911).

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NEW MANGANESE OXIDES: HYDROHAUSMANNITE AND WOODRUFFITE*

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ABSTRACT

Hydrohausmannite occurs at Franklin, New Jersey, and at Långban and Pajsberg, Sweden, as an oxidation product of pyrochroite, $\text{Mn}(\text{OH})_2$. It is identical with synthetic material prepared by Feitknecht and Marti (1945) and others by the oxidation of synthetic $\text{Mn}(\text{OH})_2$. Chemically, hydrohausmannite is a variable hydrated oxide of Mn^{2+} and Mn^{3+} , based on the structure of hausmannite, MnMn_2O_4 , in which variation in the ratio of Mn^{2+} to Mn^{3+} is compensated by a concomitant substitution of (OH) for O. Tetragonal, with $a_0 = 5.79 \text{ \AA}$, $c_0 = 9.49$; optically uniaxial negative with ω 2.055, ϵ 1.95 (Franklin). Color brownish black to iron-black.

Woodruffite occurs at Sterling Hill, New Jersey, as botryoidal masses associated with chalcophanite and zincian cryptomelane in secondary zinc ores. Dense types have $G = 3.71$ and a hardness of $4\frac{1}{2}$, with an iron-black color; also pulverulent and chocolate-brown in color. Chemical composition $(\text{Zn}, \text{Mn}^{2+})_2\text{Mn}_5^{4+}\text{O}_{12} \cdot 4\text{H}_2\text{O}$, with $\text{Zn}:\text{Mn}^{2+} = 1.54:1$.

HYDROHAUSMANNITE

Feitknecht and Marti (1945) have shown that a variable, hydrated oxide of divalent and trivalent manganese related in crystal structure to hausmannite, MnMn_2O_4 , is formed during the oxidation of synthetic manganous hydroxide. The same substance has been obtained by Dubois (1934) and others. The composition of the phase is found analytically to range at least between the limits given by the empirical formulae $\text{MnO}_{1.15} \cdot n\text{H}_2\text{O}$ and $\text{MnO}_{1.43} \cdot n\text{H}_2\text{O}$, where n is about 0.5 and includes non-essential water. Feitknecht and Marti, following the earlier work of Starke (1939) on hydrated magnetite, consider that the mechanism of compositional variation involves a variation in the Mn^{2+} to Mn^{3+} ratio in a hausmannite-like structure with valence compensation effected by a concomitant substitution of (OH) for O. The synthetic hydrated oxide is distinguished from anhydrous hausmannite by the appearance of a very strong extra line in the x -ray powder pattern. The two patterns otherwise are identical, although the high order lines of the hydrated phase are relatively diffuse. The extra line appears adjacent to and on the high- θ side of the first line, (101), in the hausmannite pattern and it is stated that it can be indexed as (002) in the hausmannite cell. The x -ray powder spacing data are not given, however, and only a line drawing of the pattern has been published.

A mineral identical with the synthetic material has been recognized

* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 340.

from three localities as an alteration product of natural manganous hydroxide, pyrochroite. The name hydrohausmannite is here adopted for the natural mineral. This name was first proposed by Feitknecht and Marti for the synthetic material. It was earlier used by Boldyrev (1928) for what appears to be the same substance; his name, however, was proposed on theoretical grounds and a specific description of a mineral was not offered.

Altered Pyrochroite and Backstromite. Synthetic $\text{Mn}(\text{OH})_2$ when freshly formed is transparent and colorless. The natural mineral, pyrochroite, always is more or less oxidized. It is then brownish black or black in color and in the final stages of alteration becomes virtually opaque. X-ray powder patterns taken in iron radiation of a number of pyrochroite specimens from Långban and Pajsberg, Sweden, and Franklin, New Jersey, show an admixture in varying proportions of two phases. One of these has a brucite-type pattern and is $\text{Mn}(\text{OH})_2$ proper; the other phase is hydrohausmannite. Completely altered crystals and, usually, the surficial parts of incompletely altered crystals give the pattern of hydrohausmannite only. The pure hydrohausmannite is iron-black to brownish black in color and affords a brown powder. It gives a distinct water test when heated in a closed tube. The material often shows a lamellar parting derived from the cleavage of the original pyrochroite. The gravity and hardness cannot be measured accurately because of the fragile and porous nature of the pseudomorphs. The small particle size and near opacity of the material precludes optical measurements. Translucent grains are dichroic in brown and dark brown.

Backstromite also gives the x-ray pattern of hydrohausmannite. The name backstromite was proposed by Aminoff (1919) for a hypothetical orthorhombic dimorph of $\text{Mn}(\text{OH})_2$ found at Långban as pseudomorphs supposedly consisting largely of manganite. The manganite had formed by the alteration of pyrochroite which itself was presumed to have formed from the original supposititious backstromite. A chemical analysis by Mauzelius of the material, cited in Table 2, was interpreted as a mixture of manganite and pyrochroite, although the presence of these substances was not shown directly. X-ray patterns of backstromite from Långban (not type material) are identical with that of hydrohausmannite.

An occurrence of what appears to be a primary crystallization of hydrohausmannite was noted on a specimen from Franklin, New Jersey. The original label of the specimen, dated August, 1911, from the F. A. Canfield collection, reads: *Unknown crystals and calcite from Franklin Furnace. These contain lots of Mn, but other tests were not made. Colonel [Colonel W. A. Roebling] or Hancock never saw a specimen like it. Price \$5.00.* The specimen shows bundles and fan-like groupings of tiny dark-

brown needles lining solution cavities a few millimeters wide in a matrix of calcite, sussexite and zincite. Optically, the mineral is uniaxial negative with indices of refraction much lower than those of hausmannite (Table 3). There is strong absorption in brown, with $E > O$, and the elongation is negative. Only about 100 mg. of material were available on the specimen. A spectrographic analysis by Dr. H. C. Harrison established that Mn was the only major cationic constituent and that Fe, Zn and other elements were present in amounts less than 0.1 per cent. The unheated sample gave an x -ray pattern identical with that of the hydrohausmannite described above. After heating in air to 500° , the extra line (002) in the pattern became very weak and the pattern then was identical with that of hausmannite with the exception of a few faint extra lines that corresponded in position to the strongest lines of the manganese spinel jacobsite.

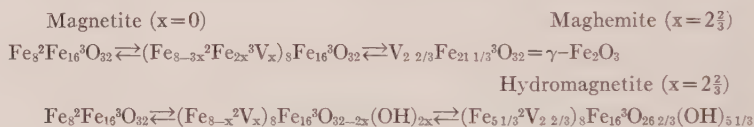
X-ray Powder Data. X-ray powder spacing data for hydrohausmannite

TABLE 1. X-RAY POWDER DATA FOR NATURAL HYDROHAUSMANNITE AND HAUSMANNITE
Fe radiation, Mn filter, 114 mm. diameter camera

Hydrohausmannite			hkl	Hausmannite	
<i>I</i>	<i>d meas.</i>	<i>d calc.</i>		<i>d meas.</i>	<i>I</i>
	Å	$a_0 = 5.79 \text{ Å},$ $c_0 = 9.49$		(Aminoff, (1926))	
2	4.95	4.94	101	4.90	2
10	4.65	4.74	002	—	—
3	3.10	3.10	112	3.09	3
2	2.89	2.90	200	2.88	1
5	2.78	2.78	103	2.75	6
6	2.50	2.50	211	2.48	10
4	2.38	2.37	004	2.35	2
3	2.05	2.05	220	2.04	2
1	1.844	1.835	204	1.824	1
2	1.803	1.804	105	1.793	2
1	1.710	1.708	312	1.702	1
1	1.655	1.648	303	1.641	1
4	1.586	1.583	321	1.577	5
5	1.549	1.550	224	1.543	5
2	1.447	1.447	400	1.441	2
—	—	—	305	1.345	1
1	1.283	1.283	413	1.278	1
1	1.231	1.236	404	1.231	1
—	—	—	127	1.197	2
—	—	—	008	1.185	2
—	—	—	415	1.122	2

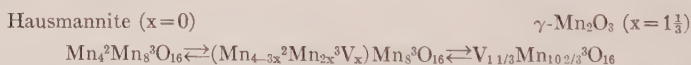
indexed in terms of a tetragonal cell with $a_0 = 5.79 \text{ \AA}$, $c_0 = 9.49$, are given in Table 1. The data differ from those of anhydrous hausmannite only in the presence of a very strong extra line that indexes as (002). The cell dimensions are virtually identical with those of hausmannite, for which Aminoff (1926) found $a_0 = 5.76 \text{ \AA}$, $c_0 = 9.44$.

Chemical Composition. Starke (1939) has shown that a hydrated type of magnetite can be synthesized in which a serial increase in the ratio of Fe^2 to Fe^3 is compensated by a concomitant entrance of both vacancies in the cation positions and a substitution of (OH) for O. This mechanism is a variant of the well known series extending between magnetite, FeFe_2O_4 , and maghemite, $\gamma\text{-Fe}_2\text{O}_3$. These two types of variation can be represented by the following formulae, in which cation vacancies are indicated by V and the subscripts indicate the unit cell contents.



In the hydrated series, other numerical relations that afford valence compensation also can be derived between the three variables, Fe^2/Fe^3 , $\text{V}/\text{total cations}$, and OH/O , and in general the particular mechanism, if this is fixed, can be identified only by chemical analysis.

Feitknecht and Marti suggest that this general type of variation obtains in hydrohausmannite, but do not discuss specific mechanisms. Hausmannite, MnMn_2O_4 , has a distorted spinel structure and, as shown by Verwey and de Boer (1936), forms an anhydrous series to the tetragonal phase, $\gamma\text{-Mn}_2\text{O}_3$:



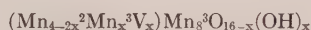
The ratio of Mn^2 to Mn^3 in synthetic hydrohausmannite is known analytically, and extends on both sides of the hausmannite ratio, $\text{Mn}^2:\text{Mn}^3 = 1:2$, but the content of essential water is not known accurately. This prevents the specific mechanism of variation from being identified. On the high Mn^2 side of the ratio, a mechanism such as $\text{Mn}^{2+}(\text{Mn}_{2-x}^{3+}\text{Mn}_x^{2+})_2\text{O}_{4-x}(\text{OH})_x$ may be operative. A similar mechanism apparently operates in the gamma polymorph of MnO_2 , and may be expressed $(\text{Mn}_{1-x}^{4+}\text{Mn}_x^{3+})\text{O}_{2-x}(\text{OH})_x$. On the high Mn^3 side of the ratio, the excess of positive valence requires either the coupled development of vacancies in the cation positions, to give the anhydrous series to $\gamma\text{-Mn}_2\text{O}_3$, or the simultaneous coupling of both vacancies and of an OH/O substitution to give a hydrated series.

The unit cell contents of the hydrohausmannite from Långban have

TABLE 2. ANALYSIS OF BACKSTROMITE (HYDROHAUSMANNITE) FROM LÅNGBAN, CITED FROM AMINOFF (1919)

		Atomic Quotients	Cell Contents (M.W. = 927)
CaO	0.14		
PbO	0.04		
MgO	1.68	Mg = .014	.132
MnO	11.59	Mn ²⁺ = .1634	1.515
Mn ₂ O ₃	77.80	Mn ³⁺ = .9856	9.138
Fe ₂ O ₃	0.14	Fe ³⁺ = .0018	.017
Sb ₂ O ₃	0.07		
H ₂ O + 130°	5.16	H+ = 5.31	5.31
H ₂ O - 130°	3.24	H- = 3.33	3.33
		O = 2.125	19.70

been calculated on the basis of Mauzelius' analysis of backstromite (Table 2), using the specific gravity, 4.84, of hausmannite. The cell contents then are approximately represented by a value $x = 1.155$ in the formula



but there is a large analytical excess of H₂O even if the water below 130° is regarded as non-essential. New analyses of coarsely crystallized synthetic or natural material of known specific gravity and unit cell dimensions are needed in order to resolve the problem of the composition of hydrohausmannite.

TABLE 3. OPTICAL PROPERTIES OF HYDROHAUSMANNITE AND RELATED MINERALS

		ω	ϵ	Reference
Hausmannite	MnMn ₂ O ₄	2.46	2.15	Larsen (1921)
Hydrohausmannite	(Mn ²⁺ , Mn ³⁺) ₃ (O, OH) ₄	2.055	1.95	(Present study)
Hetaerolite	ZnMn ₂ O ₄	2.34	2.14	Larsen (1921)
Hydrohetaerolite	(Zn, Mn ³⁺) ₃ (O, OH) ₄	2.26	2.10	Larsen (1921)

Hetaerolite, ZnMn₂O₄, is isostructural with hausmannite, MnMn₂O₄, and similarly has a hydrated analogue that has been known for many years as hydrohetaerolite (Table 3). An account of this mineral has been given by Frondel and Heinrich (1942). Hydrohetaerolite appears to be a valid species, and its composition may be determined by the same general type of mechanism obtaining in hydrohausmannite.

WOODRUFFITE

The neighboring zinc deposits of Sterling Hill and Franklin, New Jersey, are known chiefly for the primary zinc and manganese minerals

that they afford in abundance and great variety. When the Sterling Hill mine was first opened about 1870, however, a large body of secondary zinc minerals was mined in shallow pits in the limestone adjacent to the outcroppings of the primary ore. These oxidized ores consisted chiefly of hemimorphite, and magnificent drusy specimens of this mineral have been preserved in collections. The hemimorphite was associated with a zinc-rich clay called vanuxemite (a mixture according to Faust (1951)) together with minor amounts of chalcophanite and hydrohetaerolite. Both of the latter species were first described from this place. Hydrous oxides of iron and manganese also occurred as botryoidal crusts and layers and as dense to earthy masses cementing corroded fragments of franklinite and other primary minerals. Specimens of the latter material that have been preserved in mineral collections are usually found labelled as wad or psilomelane—the latter name being used in the broad, indefinite sense formerly obtaining. *X*-ray study of a number of such specimens has shown that at least two different minerals are present. One is a variety of cryptomelane containing a small amount of zinc in solid solution, and the other is a hydrated oxide of manganese and zinc that is here described as a new species under the name of woodruffite. The latter mineral occurs chiefly as masses and crusts with a botryoidal surface and a concentric, coarsely layered internal structure. The material is very fine-grained and

TABLE 4. *X*-RAY POWDER SPACING DATA FOR WOODRUFFITE AND TODOROKITE
Fe radiation, Mn filter. 114 mm. diameter camera

Woodruffite		Todorokite		Woodruffite		Todorokite	
<i>I</i>	<i>d</i> (in Å)	<i>I</i>	<i>d</i> (in Å)	<i>I</i>	<i>d</i> (in Å)	<i>I</i>	<i>d</i> (in Å)
5	9.51	10	9.65	3	1.984	1	1.981
4	6.99	$\frac{1}{2}$	7.21	1	1.922		
10	4.77	8	4.81	2	1.895		
3	4.40	3	4.46	2	1.747		
1	4.08			1	1.680		
2	3.48			2	1.660		
1	3.33			$\frac{1}{2}$	1.636		
2	3.13	4	3.20	1	1.592		
1	3.05			5	1.423	4	1.419
$\frac{1}{2}$	2.84					1	1.392
2	2.63					5	1.331
1	2.56						
4	2.466	3	2.45				
5	2.404	4	2.40				
5	2.225	4	2.216				
1	2.152	1	2.150				
2	2.131						

TABLE 5. CHEMICAL ANALYSES OF WOODRUFFITE, TODOROKITE AND A SYNTHETIC ZN, MN OXIDE

	1	2	3	4
Na ₂ O	0.06		0.21	
K ₂ O	0.55		0.54	
CaO			3.28	
BaO	0.12		2.05	
MgO	0.62		1.01	
ZnO	13.89	14.92		14.8
MnO	7.88	8.45	12.38	12.3
MnO ₂	64.27	65.73	65.58	65.9
Fe ₂ O ₃	0.26		0.20	
Al ₂ O ₃	0.14		0.28	
SiO ₂	0.86			
H ₂ O	10.48	10.90	11.28	6.0
Rem.			2.43	
Total	99.13	100.00	99.24	99.0
G	3.71		3.67	

1. Woodruffite. Sterling Hill, New Jersey. Lee C. Peck, analyst, August, 1948.

2. Theoretical Composition, (Zn, Mn)₂Mn₅O₁₂·4H₂O with Zn:Mn²⁺=1.54:1.

3. Todorokite. Todoroki mine, Hokkaido, Japan. Yoshimura (1934). Rem. is SiO₂ 0.45, P₂O₅ 0.42, SO₃ 0.28, insol. 1.28, TiO₂ tr., CO₂ tr. H₂O includes H₂O+9.72, H₂O-1.56.

4. Synthetic hydrated zinc manganese oxide described by Wadsley (1950a, 1950b).

is opaque in crushed grains. Occasionally, corroded crystals of franklinite are found embedded in the masses, and certain of the layers, usually the outermost, may contain disseminated, platy crystals of chalcophanite. Some specimens are rather hard, about $4\frac{1}{2}$, with an iron-black color and brownish streak, but the mineral also occurs as soft, almost pulverulent coatings of a chocolate-brown color. The hard material has a specific gravity of 3.71, and the fracture is smooth-conchoidal with a dull luster.

The x-ray powder spacing data, obtained in iron radiation, are given in Table 4. The x-ray pattern is rather similar to those of todorokite (Table 4) and cryptomelane. There are marked differences, however, in the relative intensities of the first few lines in these patterns. Todorokite affords a relatively diffuse pattern, as a consequence of small particle size, and a number of lines, especially in the region from d 1.98 to 1.41, which are seen visually to correspond approximately to lines in the woodruffite pattern, were too weak and diffuse to measure accurately. The todorokite pattern was obtained from an authentic specimen kindly loaned by Dr. W. F. Foshag of the U. S. National Museum, that answered exactly the original description of this mineral by Yoshimura (1934).

A chemical analysis of woodruffite by L. C. Peck is cited in Table 5, together with the reported analyses of todorokite and a synthetic hydrated oxide of zinc and manganese described by Wadsley (1950*a*, 1950*b*). Peck's analysis as originally reported gave total Mn as MnO 60.32 and oxygen 11.83 per cent. The actual valence state of the Mn in the mineral is not known, and the analysis is here given with the MnO and O recalculated as MnO and MnO₂. A spectrographic examination of the analysis sample by Dr. H. C. Harrison showed Mn and Zn as the only major cations present, with Na, K, Ba, Mg, Si, Al and Fe present in amounts less than 1 per cent and Ca, Sr, Co, Ni, Sn, Cr, Mo, V and Ti present in trace amounts. The ratios of the analysis are very close to the formula (Zn, Mn², Mg, Na, K, Ba)₂(Mn⁴, Fe³, Al)₅O₁₂·4H₂O or, essentially,



The ratios of the analysis of todorokite are slightly different, and are between those of the formula cited and the formula (Mn², Ca, Mg, Ba)Mn₃⁴O₇·2H₂O. If todorokite and woodruffite are isostructural, as is suggested by the x-ray patterns, the formulae should be analogous. The observed differences may be due to analytical error or to impurities in the analyzed sample of todorokite. The presence of 2.43 per cent total P₂O₅, SO₃, SiO₂ and insoluble in the analysis of todorokite indicates that this material was relatively impure.

Synthetic hydrated zinc manganese oxides (or hydrated zinc manganites) have been prepared recently by Feitknecht and Marti (1945) and Wadsley (1950*a*, 1950*b*). The material of Wadsley (1950*a*) was obtained by base exchange of synthetic (Na, Mn)Mn₃O₇·*n*H₂O (with Na:Mn=1:1) with a solution of ZnCl₂. Wadsley gives the formula as (Zn, Mn)Mn₃O₇·2H₂O, but the analysis, cited in Table 5, is somewhat closer to (Zn, Mn)Mn₂O₅·H₂O with Zn:Mn=1:1. An x-ray powder pattern was indexed in terms of a hexagonal cell with *a*₀=8.41 Å, *c*₀=9.8, containing four formula-units. The actual *d*-spacings are not cited, but the pattern is said to closely resemble that of (Na, Mn)Mn₃O₇·*n*H₂O for which *d*-values are given. Wadsley (1950*b*) attempted to recrystallize the material by heating it in a dilute solution of Zn and Mn chlorides in a bomb. X-ray powder study showed that at 80° a mixture of hetaerolite with some chalcophanite was formed, at 160° a mixture of hetaerolite with some hydrohetaerolite (?) and at 300° hetaerolite only. Wadsley (1950*b*) also described a synthetic calcium derivative of (Na, Mn)Mn₃O₇·*n*H₂O with the composition (Ca, Mn)Mn₄O₉·5H₂O, together with Ba, Cu and Al derivatives. The Ca compound apparently is hexagonal with the cell dimensions *a*₀=8.44, *c*₀=9.87 Å. Samson and Wadsley (1948) have described a natural occurrence at Buchan, Victoria, of a mineral appar-

ently identical with synthetic $(\text{Na}, \text{Mn})\text{Mn}_3\text{O}_7 \cdot n\text{H}_2\text{O}$. The x -ray powder data indicate that woodruffite is distinct from all of the above mentioned substances. The pattern of woodruffite is quite unlike that of chalcophanite. The composition of this mineral usually is given as $(\text{Zn}, \text{Mn})\text{Mn}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, but Samson and Wadsley (1948) have indicated that it may be $\text{ZnMn}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$.

The name woodruffite is proposed for this species after Samuel Woodruff (deceased), for many years employed as a miner by the New Jersey Zinc Company. The detailed mineralogy of Franklin and Sterling Hill is known to science very largely through the activity of local collectors in finding and preserving unusual material. Some of the famous collections from these places are those associated with the names of Canfield, Hancock, Roebling, Fowler, Losey, Kemble, and Gage. According to F. A. Canfield,¹ “. . . Woodruff worked harder to collect, and did collect more fine specimens than all the others put together. My father came next, then the two Loseys and then the Kembles.” Among the specimens known with some certainty to have come from Woodruff are the giant franklinite crystals measuring up to 7 inches on an octahedral edge that are preserved in the Canfield collection of the U. S. National Museum and also the very realistic plaster duplications of such crystals in the Harvard collection.

REFERENCES

- AMINOFF, G.: *Geol. För. Förh.*, **41**, 473 (1919).
AMINOFF, G.: *Zeits. Kryst.*, **64**, 475 (1926).
BOLDYREV, A. K.: *Kurs Opistalenoi Mineralogii, Leningrad*, Pt. 2, 97 (1928).
DUBOIS, P.: *C. R.*, **199**, 1310, 1416 (1934).
FAUST, G. T.: *Am. Mineral.*, **36**, 795 (1951).
FEITKNECHT, W., AND MARTI, W.: *Helv. Chim. Acta*, **28**, 129 (1945).
FRONDEL, C., AND HEINRICH, E. W.: *Am. Mineral.*, **27**, 48 (1942).
LARSEN, E. S.: *U. S. Geol. Surv., Bull.* **679** (1921).
SAMSON, H. R., AND WADSLEY, A. D.: *Am. Mineral.*, **33**, 695 (1948).
STARKE, K.: *Zeits. phys. Chem.*, **42B**, 159 (1939).
VERWEY, E. J. W., AND DE BOER, J. H.: *Rec. Trav. Chim. Pays-Bas*, **55**, 531 (1936).
WADSLEY, A. D.: *J. Am. Chem. Soc.*, **72**, 1781 (1950a).
WADSLEY, A. D.: *Am. Mineral.*, **35**, 485 (1950b).
YOSHIMURA, T.: *J. Fac. Sci. Hokkaido Univ.*, ser. 4, **2**, 289 (1934).

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¹ Letter to Professor Charles Palache, January 28, 1907.

THERMAL, DEHYDRATION, AND X-RAY STUDIES ON MONTMORILLONITE

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ABSTRACT

The thermal reactions, water loss and changes in crystal structure have been investigated between 500° C. and 950° C. for five montmorillonite samples with varying chemical composition.

The water loss during the first high temperature endotherm accounts for the water proposed by the Hofmann-Endell-Wilm structure. This reaction involves changes in the spacings of the x-ray diffraction lines which probably reflect symmetry differences. There is some additional water loss between the first and second high temperature endotherms with a gradual change in the spacings of the x-ray diffraction lines but no loss in the intensity of the pattern. Crystal water is essentially completely removed by the end of the second high temperature endotherm. Water loss during this endotherm may well contribute to the thermal reaction but cannot account for it. During the endotherm the intensity of the x-ray powder pattern decreases rapidly indicating breakdown of the crystal structure and the formation of a disordered state which results in an increase in entropy. Thermodynamically the effect of increased entropy can be expressed by the general equation of the third law, $dS = dq(\text{rev.})/T$, where S is entropy; T , temperature; and $dq(\text{rev.})$ heat absorbed. Thus dq increases with S and manifests itself as an endothermal reaction in the second high temperature endotherm. The exothermic reaction which follows is attributed to the formation of spinel or enstatite and partial return to an ordered state.

INTRODUCTION

The relationship between the thermal reactions of montmorillonite during differential thermal analysis and the physical and chemical changes which take place simultaneously in the sample has occupied the attention of many investigators. Some of these reactions are well understood but certain phenomena connected with the high temperature reactions remain controversial. Several theories have been proposed to account for the high temperature reactions in montmorillonite but in the opinion of the authors none have been adequately proven.

It is generally accepted that the endothermic reactions which occur between 100 and 250° C. are due to the loss of interlayer and adsorbed water and that their configuration is influenced greatly by the exchangeable cation. Nutting (1) and Page (2) have shown that the endotherm at 650–750° C. is associated with a further loss of water which accounts for most of the water remaining after loss of the low temperature types and must, therefore, be derived from the hydroxyl groups in the octahedral layer, assuming the crystal structure proposed by Hofmann-Endell-Wilm (3). Evidence has been presented by Page (2) that a small amount of water is lost beyond the 650–725° C. endotherm in some mont-

morillonites. It has been suggested that this water loss is indicated by the second high temperature endotherm (4) at 800–890° C. Various theories have been proposed to account for the presence of additional water: McConnell (4) has proposed to account for this water as discrete $(OH)_4$ groups in the tetrahedral layers; Edelman and Favejee (5) have suggested the substitution of hydroxyl groups for oxygen in the tetrahedral layer; Page (2) has suggested a relationship between this water and the high magnesium content of some montmorillonites.

The present studies have been undertaken in order to obtain a more precise explanation of the high temperature thermal reactions of montmorillonite in terms of accompanying changes in crystal structure and water losses. Experimental work has been carried out on five montmorillonite samples from Clay Spur, Wyoming; Belle Fourche, South Dakota; Little Rock, Arkansas; Plymouth, Utah; and Otay, California. These samples, which have been described by Earley, et al. (6) were sodium saturated and separated into particle size fractions by centrifugation. Fractions with particle size less than 300 $m\mu$ in equivalent spherical diameter, as calculated by Hauser's (7) modification of Stoke's law were used in each case.

APPARATUS

Differential thermal analysis studies were carried out using the equipment described by McConnell and Earley (8). The samples were dried at 65° C., ground to about 200-mesh and packed in the sample holder with a tamping action (8).

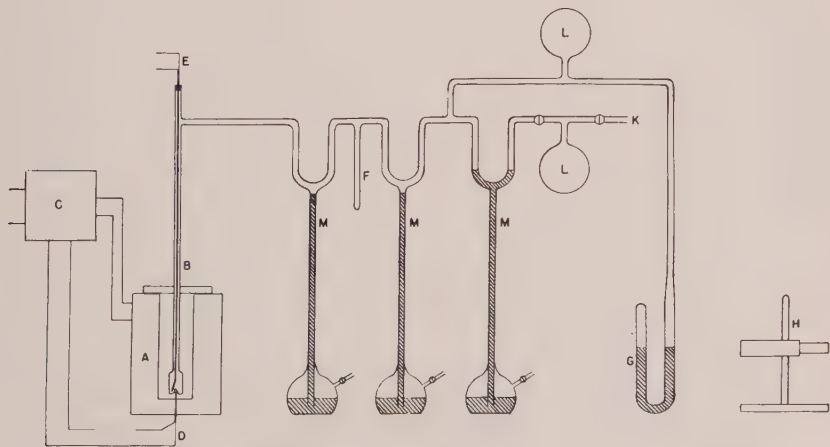


FIG. 1. Dehydration apparatus. A—Furnace, B—Reactor tube, C—Controller, D—Control thermocouple, E—Inside thermocouple, F—Freeze-out Trap, G—Mercury manometer, H—Cathetometer, K—Connection to vacuum pump, L—Reservoirs, M—Mercury traps.

X-ray powder diffraction photographs of the montmorillonite samples were obtained with Debye Scherrer type cameras of radius $180/\pi$ mm.

Dehydration studies were carried out by measuring the vapor pressure of water developed during heating of the sample in an evacuated system which is illustrated in Fig. 1. The clay sample is placed in a silica glass reactor tube which is connected to the pressure apparatus through a ground glass joint. The pressure apparatus is equipped with a freeze-out trap which permits a reduction of the water vapor pressure to about 0.1 mm. when the trap is surrounded by a mixture of ethyl alcohol and dry ice. Mercury traps are used to isolate the freeze-out trap and to separate a calibrated reservoir from the rest of the system. The traps permit separation of various parts of the system without movement of stopcocks and act as sensitive indicators of leaks which may develop. The system is sealed to a mercury manometer with which the pressure in the system is measured to ± 0.02 mm. by means of a cathetometer. The calibrated reservoir is used to determine the total volume of the pressure system. The temperature of the sample in the reactor is measured by a thermocouple which extends from the bottom of the surrounding furnace into a recess in the base of the reactor tube. A second thermocouple inserted inside the reactor tube and touching the sample was found necessary in certain experiments to record sample temperatures more accurately.

Two procedures were used in the dehydration experiments. In the first the sample was heated by a surrounding furnace in suitable increments with the temperature being held at each point by a controller until no further increase in pressure was noted over a twenty-four hour period. During these runs the water vapor pressure over the sample was kept as near to zero as possible by means of a freeze-out; during measurement of the pressure in the system the sample was closed off from the rest of the apparatus by a mercury trap. The attainment of equilibrium at any one temperature and zero pressure required up to five days. In the second method of dehydration study the sample was heated at approximately $10^\circ\text{C. per minute}$ using a model *S* micromax recorder (0° – 1400°C. uniform scale for Pt-Pt 10 per cent Rh), a controller and timer. The sample temperatures were obtained from the inside thermocouple and readings of temperature and cumulative pressures were recorded at one or two minute intervals.

EXPERIMENTAL RESULTS

The five purified montmorillonite samples were analyzed by differential thermal analysis using a recording sensitivity of ± 2.5 microvolts per chart division and a heating rate of $10^\circ\text{C. per minute}$. The thermal curves shown in Fig. 2 are described by Earley, et al. (6). The materials from

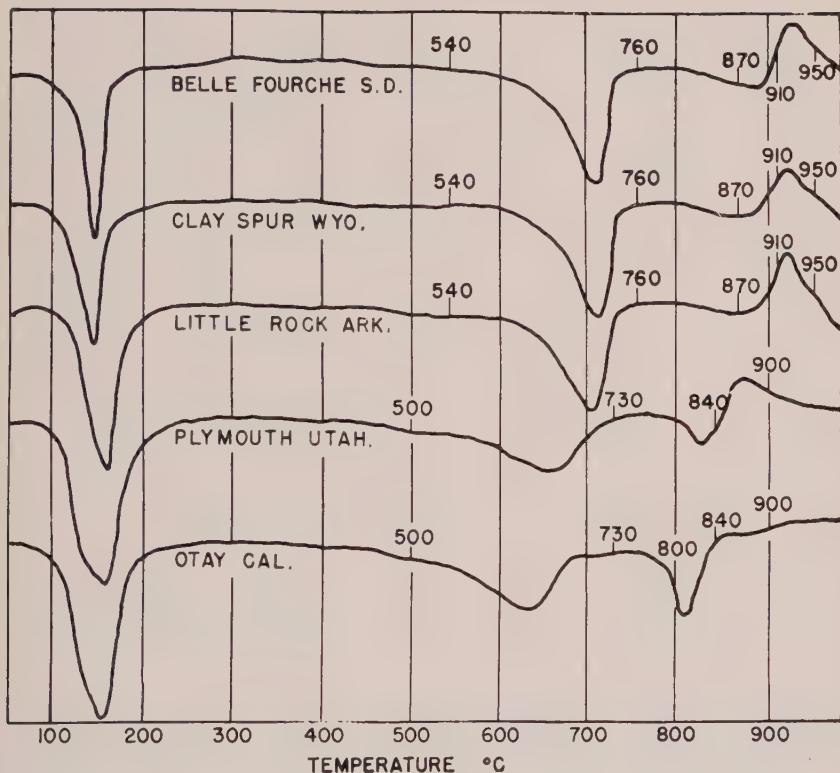


FIG. 2. Differential thermal curves of sodium saturated montmorillonites; Pt/Pt 10% Rh thermocouples.

Belle Fourche, Clay Spur, and Little Rock give very similar results, showing a marked endotherm at 710–715° C., a small broad endotherm at 880–885° C., followed by a pronounced exotherm at 925–930° C. The Plymouth and Otay samples show much lower temperatures for all of their thermal reactions. Both of these materials give well defined second high temperature endotherms at 820–830° C. The Plymouth material gives an exotherm at 870° C. while the Otay sample shows an exothermic drift above 850° C.

To study the changes which take place in montmorillonite during thermal reactions, samples were heated in the DTA equipment to the temperatures indicated in Fig. 2 and quenched in an air stream. In this way it was possible to heat a sample to a precise reaction point, stop the reaction, and study the phase or phases by *x*-ray diffraction. The material used for *x*-ray study was carefully taken from the area nearest the thermocouple in order to eliminate the effect of thermal gradients within

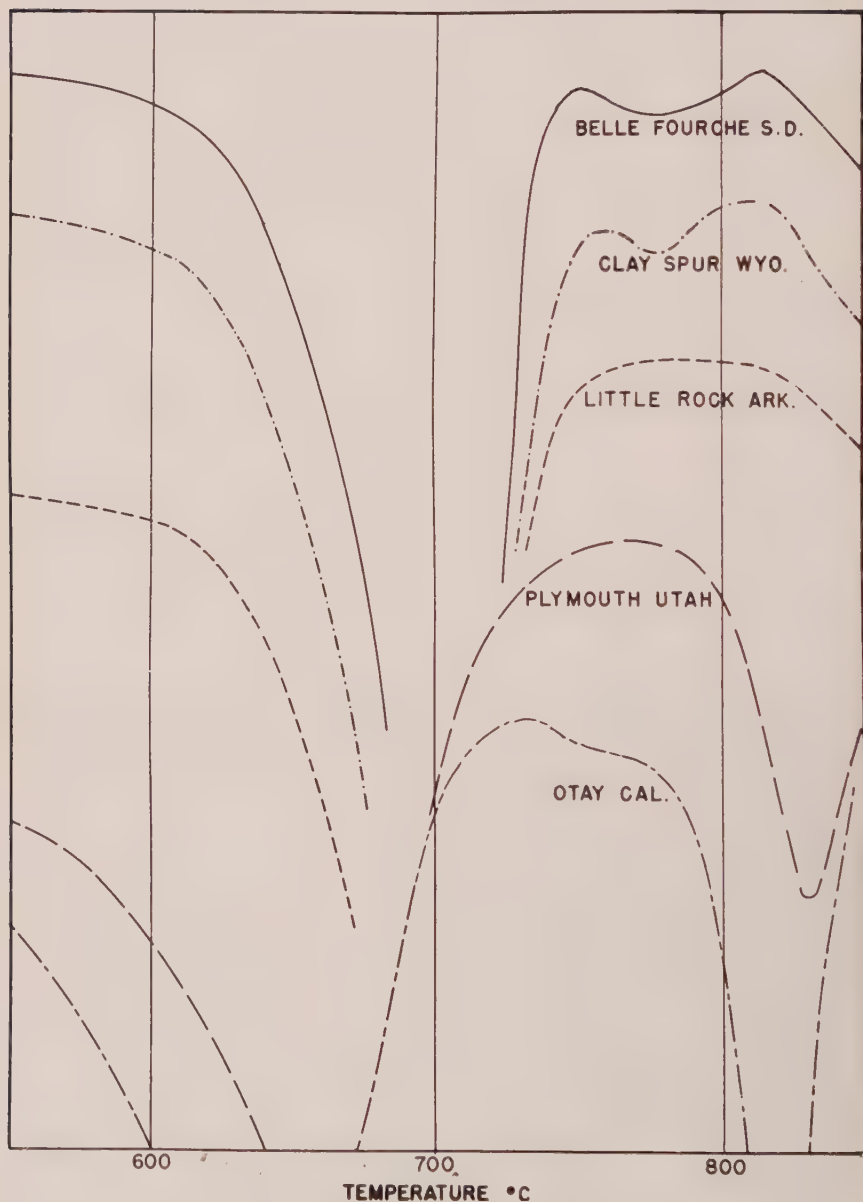


FIG. 3. Portions of differential thermal curves of sodium saturated montmorillonites obtained at maximum sensitivity.

the sample and thus the state of reaction should correspond closely with the recorded thermal state. In addition to these thermal analyses, each of the montmorillonites was thermally analyzed at the maximum sensitivity of the recorder (± 0.25 microvolts per chart division). Portions of these *DTA* curves in the vicinity of the first high temperature endotherm ($600\text{--}800^\circ\text{C.}$) are shown in Fig. 3. With this sensitivity this endothermic reaction is off scale in each case, but a minor endotherm is given by the Belle Fourche, Clay Spur, and Otay samples immediately after the first high temperature endotherm; this minor endotherm is not shown by the Little Rock and Plymouth samples. The significance of this reaction will be considered later in this paper in terms of *x*-ray diffraction and dehydration results.

X-ray powder diffraction studies have been carried out on samples heated to the temperatures indicated in Fig. 2. A detailed study of the diffraction photographs has permitted a correlation of structural changes with thermal reactions. The *x*-ray powder diffraction photographs of the Little Rock samples have been reproduced in Fig. 4 and the diffraction data from these photographs are given in Table 1.

From Table 1 it will be seen that at 540°C. , before the first high temperature endotherm, the clay appears to be unchanged from its condition at room temperature. It has absorbed some of the organic liquid used as

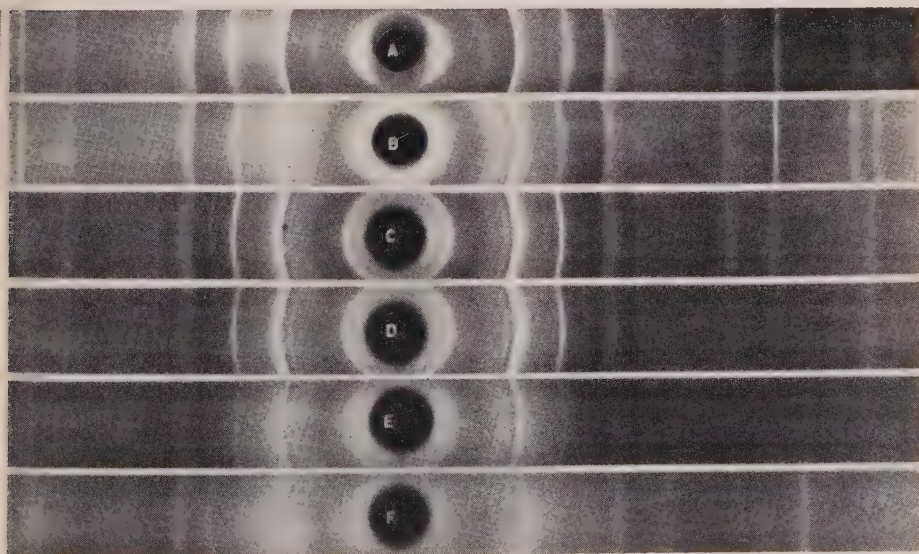


FIG. 4. *X*-ray powder photographs of sodium saturated montmorillonite, Little Rock, Arkansas, after heating in *DTA* equipment. $\text{FeK}\alpha$ radiation; camera radius, $180/\pi$ mm. A—Unheated, B— 540°C. , C— 760°C. , D— 870°C. , E— 910°C. , F— 950°C.

TABLE 1. X-RAY DIFFRACTION DATA (FeK α RADIATION) SODIUM SATURATED MONT-MORILLONITE—LITTLE ROCK, ARKANSAS (<300m μ FRACTION) HEATED IN DIFFERENTIAL THERMAL ANALYSIS EQUIPMENT

540° C.	760° C.	870° C.	910° C.	950° C.	Interpretation
<i>I</i> <i>d</i> Å	<i>I</i> <i>d</i> Å	<i>I</i> <i>d</i> Å	<i>I</i> <i>d</i> Å	<i>I</i> <i>d</i> Å	
10 <i>b</i> 12.9					(001) Expanded
	6 9.83	7 9.75	7 9.74		(001) Anhyd. mont.
1 <i>b</i> 6.55					(002) Expanded
	2 4.86	2 4.79	2 4.79		(002) Anhyd.
7 4.51	10 4.48	10 4.45	10 4.44		(110) (020)
1 4.32					(003) Expanded
				1 4.29	<i>Spinel</i>
1 4.12	1 4.14	1 4.10	2 4.09	10 4.11	Cristobalite
	1 3.73				?
	1 3.56	$\frac{1}{2}$ <i>b</i> 3.53	1 3.53		K β (003) Anhyd.
2 3.25					(004) Expanded
	5 3.23	4 3.23	5 3.23		(003) Anhyd.
	2 2.86	1 2.87	2 2.85		?
		1 2.83			?
				2 2.81	<i>Spinel</i>
2 <i>b</i> 2.58	2 <i>b</i> 2.59	1 2.57			(130) (200)
				1 2.53	?
	1 2.482	1 2.474			?
			1 <i>b</i> 2.459	5 <i>b</i> 2.437	<i>Spinel</i>
$\frac{1}{2}$ 2.245	2 2.242	2 2.232	1 2.222		(220) (040)
				1 2.011	<i>Spinel</i>
		1 1.999	$\frac{1}{2}$ 1.990		?
	$\frac{1}{2}$ 1.938	$\frac{1}{2}$ 1.936			?
$\frac{1}{2}$ 1.876					(007) Expanded
	$\frac{1}{2}$ 1.750				?
	1 1.732	1 1.744	1 1.746		?
2 1.700					(240) (310) (150)
	1 <i>b</i> 1.681	1 1.685	1 1.677		?
				1 <i>b</i> 1.542	<i>Spinel</i>
	1 1.522	1 1.527	$\frac{1}{2}$ 1.523		?
4 1.503					(330) (060)
	1 1.495	1 1.495			?
			2 <i>b</i> 1.414	4 <i>b</i> 1.421	<i>Spinel</i>
1 <i>b</i> 1.293	1 1.321	1 1.332	2 1.326		(260) (400)
1 1.251	1 1.249	1 <i>b</i> 1.262	$\frac{1}{2}$ 1.258		(350) (170) (420)

a mounting medium in preparation of the specimen to give an expanded "c" dimension of 12.9 Å. A further test which was carried out showed that this material also will absorb interlayer water to give a 12.6 Å basal spacing. At 760° C., past the first high temperature endotherm, the clay will no longer expand with water or organic liquids and gives a basal

spacing of 9.8 Å. Some structural change has taken place as would be expected with the loss of the hydroxyl groups, such that the (110) (020) diffraction line at 4.50 Å is now reduced to 4.47 Å and other lines of the normal clay pattern are split into doublets and reduced in intensity. Without trying to analyze the precise nature of the structural changes it may be said that the new structure has different "a" and "b" dimensions and probably a different symmetry. This modification of the montmorillonite structure has been referred to by Bradley and Grim (9) as the anhydride phase of montmorillonite. In this paper the anhydride phase will be referred to as anhydrous montmorillonite.

At 870° C. near the minimum of the second endotherm a further change is apparent in the same direction as observed at 760° C. The (110) (020) spacing is further reduced to 4.45 Å and lines already resolved into doublets are spread farther apart. At 910° C. between the second endotherm and the exotherm, anhydrous montmorillonite diffraction lines are still evident but much reduced in intensity and two spinel diffraction lines have appeared. It seems apparent that the decrease in the intensity of the anhydrous montmorillonite diffraction pattern at this point, which reflects a breakdown of the structure, must be related to the second high temperature endotherm. The formation of an amorphous or disordered state from a crystalline one must be accompanied by an increase in the entropy of the sample. According to the third law of thermodynamics, $dS = dq \text{ (rev.)} / T$, where S is entropy; T , temperature, and $dq \text{ (rev.)}$ is reversible heat absorbed, an increase in entropy is accompanied by an absorption of heat. Thus the breakdown of the anhydrous montmorillonite structure can account for the second high temperature endotherm, without the necessity of any accompanying water loss.

In the case of the Little Rock sample the second endotherm is followed immediately by an exotherm which coincides with the appearance of spinel in the sample. It must be concluded that spinel formation accounts for this exotherm. Spinel formation begins before complete destruction of the anhydrous montmorillonite and the exotherm may have modified the shape of the preceding endotherm.

It will be observed that a diffraction line of cristobalite is present in all of the Little Rock samples as recorded in Table 1. The cristobalite is an impurity which could not be removed in the purification process. The quantity of this material as determined by the intensity of the diffraction line did not appear to change at any of the temperatures.

The samples from Belle Fourche and Clay Spur gave results very similar to those recorded for the Little Rock sample. In the case of the Plymouth material the thermal reactions occur at lower temperatures but the general relationship between structure and thermal properties

remains constant. The material remains unchanged up to the first high temperature endotherm and then passes into the anhydrous modification. At this point the (110) (020) spacing becomes smaller as in the previous samples, but the development of doublets from other normal montmorillonite lines has not been observed. The second high temperature endotherm coincides with the disappearance of the anhydrous montmorillonite diffraction pattern and spinel is very evident at temperatures beyond the exotherm.

The Otay montmorillonite also shows similar x-ray diffraction changes related to the thermal reactions up to the exothermic drift at 850° C. At

TABLE 2. SUMMARY OF THERMAL REACTION PRODUCTS OF MONTMORILLONITES

Temperature	Relationship With Thermal Reactions	Phases Present				
		Belle Fourche	Clay Spur	Little Rock	Plymouth	Otay
500° C.	Before 1st H.T. endo.				Normal mont.	Normal mont.
540° C.	Before 1st H.T. endo.	Normal mont.	Normal mont.	Normal mont.		
730° C.	Past 1st H.T. endo.				Anhyd. mont.	Anhyd. mont.
760° C.	Past 1st H.T. endo.	Anhyd. mont.	Anhyd. mont.	Anhyd. mont.		
800° C.	Within 2nd H.T. endo. before minimum					Anhyd. mont.
840° C.	Half way out of 2nd H.T. endo.				Minor anhyd. mont. +amorph.	
840° C.	Just beyond 2nd H.T. endo.					Minor enstatite +amorph.
870° C.	Near minimum of 2nd H.T. endo.	Anhyd. mont.	Anhyd. mont.	Anhyd. mont.		
900° C.	Beyond H.T. endo.				Spinel +amorph.	
900° C.	Within exo. drift					Increased enstatite +amorph.
910° C.	Half-way out of 2nd H.T. endo.	Weak anhyd. mont. +amorph.				
910° C.	Almost out of 2nd H.T. endo.		Weak anhyd. mont. +amorph. +weak spinel	Weak anhyd. mont. +amorph. +weak spinel		
950° C.	Beyond H.T. exo.	Spinel +amorph.	Spinel +amorph.	Spinel +amorph.		
1000° C.	Within exo. drift					Enstatite +cristobalite +amorph.

this point the anhydrous montmorillonite structure has disappeared and a new pattern appears which increases in intensity and number of lines at 900° C. and again at 1000° C. This phase has been tentatively identified as enstatite. At 1000° C. a very small amount of cristobalite has developed. The phases present in each of the samples at various temperatures between 500° C. and 1000° C. are given in Table 2.

Dehydration studies were carried out on each of the samples with the same rate of heating as used in differential thermal analysis. However, the dehydration experiments were carried out at pressures not over 20 mm. while in thermal analysis the experiments were carried out at atmospheric pressure. This difference in pressure is likely to result in reducing the temperature at which water is recovered during dehydration. The differences should not be great because the partial pressure of water vapor over the sample during thermal analysis will not be great at elevated temperatures although it may be appreciable in the sample during water loss reactions since there is a definite interval of time between the release of the hydroxyls and the removal of water from the sample. Thus, the temperature of the endotherm peak does not coincide precisely with the greatest rate of pressure increase in the dehydration experiments. It is assumed that the steepest part of the dehydration curves, Figs. 5 and 6, corresponds to the peak of the endothermal reaction. If this assumption is correct there is about a 40° C. difference between the reaction temperature as given by thermal and dehydration analysis. Figures 5 and 6 show the dehydration curves for each of the five samples heated at 10° C. per minute. From these curves it is apparent that there is a small but real increment of water released after the main water loss in the Otay, Belle Fourche, and Clay Spur samples, but not in the Plymouth or Little Rock samples. It is proposed that this small increment of water is the cause of the small endothermal reaction after the first high temperature endotherm in the same samples.

To examine the effect of rate of heating and partial pressure of water vapor on water loss a sample of the Plymouth montmorillonite was heated to predetermined temperatures until all of the water was removed at each temperature. This curve, Fig. 6, in general, has the same shape as that of the 10° C. per minute run except that the octahedral water appears to come out of the structure as low as possibly 150° C. and is virtually all removed at 600° C., a much lower temperature than in the other experiments. In this curve it is interesting to note that if one takes the water removed above 150° C., the inflection point of the curve, this water accounts for 4.96% of the sample weight at 150° C. This value is in fair agreement with the water content (4.77%) computed from the chemical analysis of the material assuming the Hofmann-Endell-Wilm

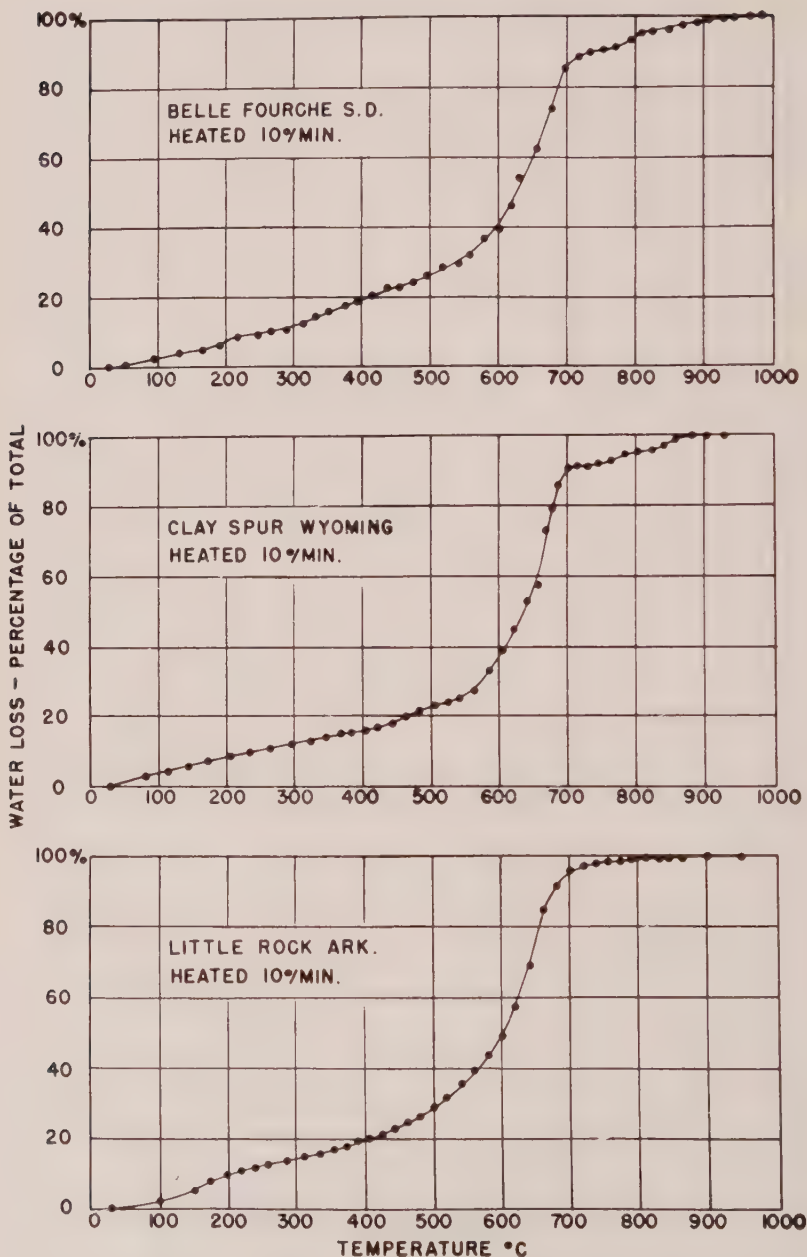


FIG. 5. Dehydration curves of sodium saturated montmorillonites.

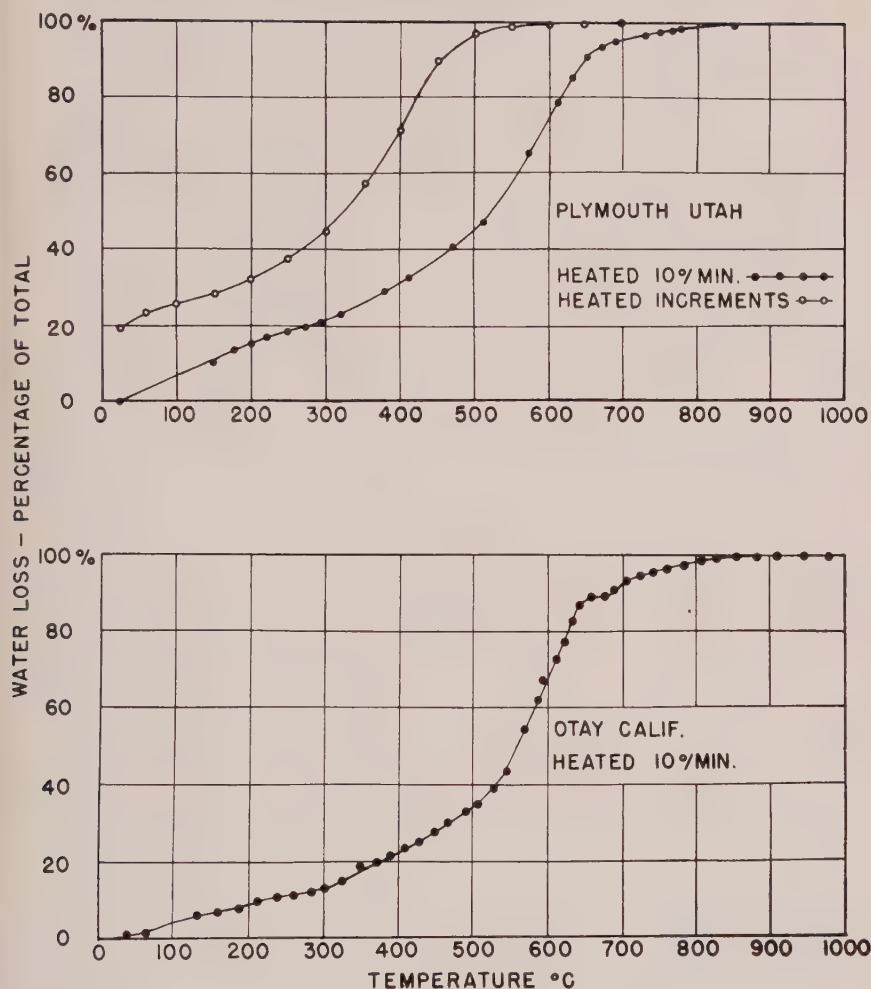


FIG. 6. Dehydration curves of sodium saturated montmorillonites.

structure. None of the dehydration curves show a significant water loss in the region of the second high temperature endotherm. It is true that there is some water coming off in this region but the amount is exceedingly small and removal takes place at a nearly uniformly decreasing rate. Further, the temperature at which the water is completely removed corresponds with the end of the second high temperature endotherm and the breakdown of the montmorillonite structure as evidenced by *x*-ray examination. Thus, the second high temperature endotherm can scarcely be due to the removal of water from the crystal structure.

DISCUSSION

A comparison of the *DTA* curves and the *x*-ray diffraction patterns obtained at different temperatures confirms the findings of Bradley and Grim (9) that an anhydrous phase which is structurally different is present after the first high temperature endotherm. This phase is inert to layer absorption of liquids. No evidence of an expansion of (001) was observed in this phase as compared with (001) of montmorillonite dried at temperatures below the first high temperature endotherm. This behavior is common to the five clay samples examined although some minor details differ.

There is no doubt that in these samples the second high temperature endotherm is associated with the breakdown of the anhydrous clay structure. During this reaction the *x*-ray films show a loss of intensity of clay lines and in the following exotherm, spinel or enstatite lines appear. Where enstatite is formed (Otay), a distinct exotherm is not apparent and this can only be associated with the formation rate and energy of this mineral. As pointed out by Bradley and Grim (9) investigation has shown that the crystallization processes accompanying enstatite formation do not give distinct thermal effects.

The formation of enstatite from Otay montmorillonite has been unique in this investigation. Enstatite has been mentioned by Bradley and Grim (9) as forming during the firing of high magnesium montmorillonites. It is interesting to note that the first product of recrystallization here involves both the tetrahedral and octahedral layers. At 1000° C. this clay shows the development of minor cristobalite. In the other clays, spinel is formed, presumably from the octahedral layer constituents. The Otay clay has both a high magnesium content and a very low substitution of aluminum for silica (6) either of which may influence the formation of recrystallized products.

The water given off by the Clay Spur, Belle Fourche, and Otay montmorillonites after the prominent water loss corresponding to the first high temperature endotherm remains largely unexplained. It has not been possible to correlate the presence or absence of this small increment of water with any properties of this group of montmorillonites as described by Earley, et al (6). The suggestion of Page (2) that this water is directly related to the magnesium content of the montmorillonite has not been substantiated. This is illustrated by the fact that the Belle Fourche and Otay materials have low and high magnesium contents respectively and do contain the additional water while the Plymouth sample with an intermediate magnesium content does not contain this water. The dehydration curves (Figs. 5 and 6) indicate that the additional water is lost before the second high temperature endotherm and the breakdown of the

anhydrous clay structure. The lack of relationship between this water loss and the second high temperature endotherm is further illustrated by the Plymouth sample which has a very distinct second high temperature endotherm but does not lose any additional water.

Possible explanations for this small increment of water beyond the normal hydroxyl groups of the octahedral layer are provided for by the $(\text{OH})_4$ tetrahedral groups of McConnell (4) or the (OH) groups in the tetrahedral layer suggested by Edelman and Favejee (5). However, the apparent lack of correlation between this increment of water and other properties of montmorillonite suggests that this water is more likely due to small amounts of an unidentified impurity which has been concentrated in the purified samples or created in the purification process. The lack of identification may be due to a colloidal nature of the impurity or to its close association with the montmorillonite in a mixed layer structure.

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Dr. Paul D. Foote, Executive Vice President of the Gulf Research & Development Company granted permission to publish these results.

REFERENCES

1. NUTTING, P. G., Some standard dehydration curves of minerals: *U.S.G.S., Professional Paper 197-E* (1943).
2. PAGE, J. B., Differential thermal analysis of montmorillonite: *Soil Sci.*, **56**, 273-283 (1943).
3. HOFMANN, U., ENDELL, K., AND WILM, D., The crystal structure and the swelling of montmorillonite: *Zeits. Krist.*, **86-A**, 340-348 (1933).
4. MCCONNELL, DUNCAN, The crystal chemistry of montmorillonite: *Am. Mineral.*, **35**, 166-172 (1950).
5. EDELMAN, C. H., AND FAVEJEE, J. C. L., On the crystal structure of montmorillonite and halloysite: *Zeits. Krist.*, **102-A**, 417-431 (1940).
6. EARLEY, J. W., OSTHAUS, B. B., AND MILNE, I. H., Purification and properties of montmorillonite: *Am. Mineral.*, **38**, 707-724 (1953).
7. HAUSER, E. A., AND REED, C. E., Studies in thixotropy. I. Development of a new method for measuring particle size distribution in colloidal systems: *Jour. Phys. Chem.*, **40**, 1169-1182 (1951).
8. MCCONNELL, DUNCAN, AND EARLEY, J. W., Apparatus for differential thermal analysis: *Jour. Am. Cer. Soc.*, **34**, 183-187 (1951).
9. BRADLEY, W. F., AND GRIM, R. E., High temperature thermal effects of clay and related materials: *Am. Mineral.*, **36**, 182-201 (1951).

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IN DEFENSE OF THE SECOND DECIMAL

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ABSTRACT

Synthetic and practical examples are used to show that excessive rounding must be avoided whenever quantitative results are to be subjected to extended numerical analysis. In work reporting original measurements it is usually preferable to record the complete observation. Where this is not desirable, it should always be possible for an interested reader to reclaim the original observations. This can not be done if the hundredths place is rounded out of conventional silicate analyses or the tenths place is rounded out of modal analyses.

The problem of the extent to which measurements are to be carried and recorded plagues every natural science and has no general solution. In fact, it is not a general problem at all, but an infinite family of specific problems, each of which must be faced in its own context. Basically these problems are psychological, and the mathematical or physical conventions we adopt in treating them reflect the demands of the situations which give rise to them.

For a long time petrologists and mineralogists seem to have been unduly impressed by the precision of chemical analysis. As late as the first decade of the 20th century, silicate analyses were not infrequently stated to three places, and sometimes a fourth was added for good measure. The pendulum has now swung the other way; and in a summary of the most extensive study of the reproducibility of silicate analyses so far made, the standard practice of quoting through the second place has been strongly questioned (Fairbairn, 1951). Recently a similar attack has been made on the fairly common practice of retaining the first decimal in statements of modal analyses (Hamilton, 1952). These objections reflect a rather widespread skepticism but are based on reasoning which I feel is not applicable. Both Fairbairn and Hamilton base their argument on the *interpretation* of measurements, and while this is no doubt a major consideration for every reader, the immediate problem facing the the author of the measurements is their *presentation*.

In the standard rock analysis, weighings are recorded to the "nearest tenth" of a milligram and the principal fusion, out of which come the values for silica, alumina, lime, magnesia, titania, and total iron, is carried through on a one gram sample. A tenth of a milligram is one hundredth of a per cent of a gram, and when the chemist tells us that he finds 73.24 per cent of silica in a rock, he is telling us what he has observed. He does not say that he or any other chemist would get exactly 73.24 per cent on a second sample, but *only that he got 73.24 per cent on this one*. If he reported 73.241, he would be telling us more than he could

possibly observe in a single analysis. If he reported 73.2 he would not be telling us all that he observed, and that, after all, is the first thing we want to know.

Before asking him to run the analysis we probably guessed that the sample contained between 70 and 75 per cent of silica, and he probably was informed of this guess. We assume that composition is a continuous variable; and in asserting that the sample carries between 70 and 75 per cent of silica, we imply that the true silica *may* have any value whatever—to any number of decimals—between 70.000. . . and 75.000. . . . The analyst's position is a little different. It is his job to make observations, not assumptions, and he has no way of making direct observations past the second decimal place unless he works on a 10 gram sample. Even when he is favored by a large gravimetric factor, as when he weighs magnesium phosphate and reports MgO, the last entry which may have any value at all between 0 and 9 is the hundredths place. To him this is the observational limit of continuity, and quite sensibly he records his result to that limit. This is what we want him to do, or what we should want him to do.

For reasons concerned more with the interpretation than the presentation of data, Dr. Fairbairn (1951, p. 70) feels that we “. . . should ruthlessly discard unnecessary detail beyond the decimal point,” and the sense of my own contribution to Bulletin 980 (Fairbairn 1951, p. 64) is the same, though the wording is less forthright. On reconsideration, however, I am convinced that from the point of view of representation—a point of view too seldom considered by geologists—the premature mutilation of the chemist's report is most unwise. And whether for interpretive purposes the detail beyond the decimal point is unnecessary, whether, in fact, it is to be regarded as detail at all, will depend entirely on what information we wish to obtain from the data and how we propose to obtain it.

Dr. Hamilton's argument that modal analyses should not be quoted beyond the nearest per cent is based on the same reasoning which led to Dr. Fairbairn's explicit and my implicit dictum concerning the hundredths place in chemical analyses. It is open to somewhat the same objection, and for one of my experience it is much simpler to examine the problem in terms of modal analysis. The discussion which follows, therefore, centers on the advisability of retaining the first place after the decimal in modal analysis; but most of the argument is directly applicable to the question of whether or not the second place should be retained in conventional silicate analyses.

For count lengths between 1500 and 2000 points the theoretical precision for major constituents, as a standard deviation, is about 1 per cent

of the whole. There is thus some justification for discarding the tenths, and this is particularly so if we merely wish to scan the table and declare solemnly that the rock either is or is not "variable." But the validity of the table *as a record of the observations* is impaired by this process, and if any serious evaluation of the data is to be attempted the results may vary widely and erratically depending on whether the calculations have been performed before or after rounding.

Suppose, for instance, that an analysis of count-length 1502 yields the frequencies

Quartz	449
Microcline	502
Plagioclase	530
Biotite	21

A single count is $1/1502$ or .03 per cent of the whole. In the hundredths place the analysis thus moves in units of .03, and the first entry which may have any value regardless of its neighbor to the left is in the tenths column. When we see a value of 10.03 per cent, for instance, we immediately assume that it *might* have been 10.02 or 10.04, and much of the meaning we attach to the result is based on this assumption. But for our chosen count length the two nearest neighbors of 10.03 are 10.00 and 10.06. The entry in the tenths place controls the entry in the hundredths. But the entry in the tenths place is not at all influenced by that in the per cent column; what we may call the "continuous least count" of the procedure is thus 0.1 per cent, just as it is 0.01 per cent in the standard silicate analysis. Reducing the observed frequencies to the nearest relative least count we have:

Quartz	29.9
Microcline	33.4
Plagioclase	35.3
Biotite	1.4

With the tenths rounded out this becomes:

Quartz	30
Microcline	33
Plagioclase	35
Biotite	1

which gives a total of 99. Now if the table is to be an adequate record of the observations, we must be able to reclaim the original frequencies from it. This may be attempted in any of three ways. First, we may simply ignore the missing 1 per cent. Alternatively, we may "recalculate" the recorded analysis to 100 before reconstructing the observed frequencies, and this may be done in either of two ways. If we are still adamant about the tenths place, we merely assign the missing per cent to the largest

value, plagioclase. We may feel, however, that our calculation is to be preferred to the analyst's observation, and in this event we shall regain the lost per cent by adding 4 parts of it to plagioclase and 3 each to quartz and microcline. (In fact every one of these procedures assumes that guessing is better than observing, but the assumption is more obvious in the last case.)

Frequencies reconstructed from the original statement and each of the rounded versions are shown in Table 1. If the tenths place is left

TABLE 1. OBSERVED AND RECONSTRUCTED FREQUENCIES

Mineral	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>
Quartz	449	449	451	451	456
Microcline	502	502	496	496	500
Plagioclase	530	530	526	541	532
Biotite	21	21	15	15	15

A—Observed.

B—Recalculated from total and percentages carried to tenths.

C—Recalculated from total and rounded percentages, ignoring closure error.

D—Recalculated from total and rounded percentages, assigning lost per cent to most abundant constituent.

E—Recalculated from total and rounded percentages, distributing lost per cent over three major constituents.

standing in the analysis, the combination of total count-length and percentage composition permits reconstruction of the observed frequencies, so that the frequencies themselves need not be recorded. If the tenths place is rounded out,¹ the observations can not be reclaimed correctly from the table. If we then want to know what the analyst found—something the table is supposed to tell us—we must write him a letter.

It may be argued, and no doubt for specific purposes it is sometimes true, that whether the analyst recorded 526 or 541 counts of plagioclase, or 15 or 21 counts of biotite, is a rather trivial affair. Correct as it may be in particular cases, however, this attitude betrays a fundamental lack of sympathy for the relation between tables which record data and arguments which interpret them. Rounding which makes recovery of the original observations impossible is a form of interpretation and should be done by text discussion, by separate tables, or not at all. But the writer presenting original data will have fallen short of his responsibility if an interested reader can neither find the measurements nor reclaim them from information recorded in the paper. If a table of percentages is to provide an adequate record of observations, most of the conventional

¹ 5's have been rounded to the nearest number.

rounding, e.g. rounding dictated by the results rather than the experimental procedure, must be left for the reader to do. The comforting sense of superiority which creeps over us when we examine unrounded results published by others is suitable recompense for our performance of this service.

Regarding a table simply as a description or record, the damage done by excessive rounding may be summarized as a blurring or actual deletion of the observations. If we plan to do more than publish or inspect the table, however, the effects of over-rounding may be far more complex.

Suppose we are given a string of ten results differing by 0.1, e.g.,

$$60.1, 60.2, 60.3, \dots, 61.0.$$

The standard deviation for such a run is 0.303 and does not vary with the numbers to the left of the decimal point, or with the first number of the string on the right. Thus the series $hk \cdot 0 \dots hk \cdot 9$ has exactly the same standard deviation as the series $hk \cdot 5 \dots h(k+1) \cdot 4$. This holds for any index of dispersion and is the basis for the coding procedures which so often facilitate extended numerical analysis. If the tenths place is rounded out, each entry in the series becomes hk or $h(k+1)$, and if we next subtract hk from each member, any such series is resolved into a run of 0's followed by a run of 1's which, we may represent by

$$x(0)y(1),$$

where $0 \leq x \leq 10$ and $y = 10 - x$. The series we began with would now be written

$$0, 0, 0, 0, 0, 1, 1, 1, 1, \text{ or } 5(0)5(1).$$

The standard deviation of the rounded run obviously varies with the value of x , and this in turn is controlled by the first term, in the fashion shown in Table 2.

TABLE 2. EFFECT OF FIRST TERM OF SERIES ON VARIANCE (V) AND STANDARD DEVIATION (s)

1st term	x	y	V	s
$hk.0$	5	5	.278	.527
$hk.1$	4	6	.267	.516
$hk.2$	3	7	.233	.483
$hk.3$	2	8	.178	.422
$hk.4$	1	9	.100	.316
$hk.5$	0	10	0	0

If in a group of such series the initial terms are equally likely, a condition which could be met only if the continuous least count of the pro-

cedure yielding them were not larger than 0.1, the average variance obtained after rounding would be .183 as compared with .092 computed directly from any one of the unrounded series *regardless of its initial term*. This would amount to an average upward bias of more than 30 per cent in the standard deviation, produced entirely by rounding. If this bias were constant we might even accept it as providing an extra margin of safety in certain situations. But this is very clearly not the case; rounding will sometimes lead to an underestimate of dispersion and will quite frequently overstate it by considerably more than the long run average of 30 per cent. In fact, the probability of obtaining the exact average bias in a single run is zero.

TABLE 3. BIOTITE VALUES, WESTERLY TEST STRIP*

2.7	2.2	3.0	3.4
3.1	3.8	4.2	3.8
3.7	3.5	3.2	3.3
2.3	3.2	2.7	2.8

* From Table 25, *U. S. Geol. Survey, Bull.*, 980.

This example is of course highly synthetic. The result could be generalized by repeated enumeration and summation, but the procedure would no doubt alienate most of the audience for which this note is intended, without making any original contribution to analysis of the purely statistical problem involved. On the whole it will be best to leave mathematics to the mathematicians and pass at once to a practical illustration. Modal analyses of the test strip of Westerly granite, used as one of the materials in the analytical testing program described in Bulletin 980 and cited by Dr. Hamilton as a particularly egregious instance of "pseudo-precision," will serve as an example. The biotite values recorded in Table 25 (p. 61) of the Bulletin are shown below in Table 3. The mean biotite content for the strip is 3.2 per cent, the standard deviation calculated from the unrounded data—e.g. the data recorded to the continuous least count—is 0.5552 per cent, and the variance is 0.3083.

As with the hypothetical example, we round the data as recorded, add 0.1 to each of the original values and round again, add 0.2 and round once more, and so forth. From each rounded series we next calculate the variance and standard deviation. The results are shown in Table 4.

The measurements were made in an attempt to detect inhomogeneities in the test material prior to crushing. Do the data of Table 3 indicate significant sample variation with regard to biotite content? The theoretical analytical error of the counting procedure is binomial, and for an

TABLE 4. EFFECT OF ROUNDING ON VARIANCE (V) AND STANDARD DEVIATION (s) OF DATA IN TABLE 3

	V	s
Original data, unrounded	.3083	.555
Original data, rounded	.4292	.655**
Original data plus 0.1 and rounded	.4667	.684**
Original data plus 0.2 and rounded	.4958	.704**
Original data plus 0.3 and rounded	.4000	.632*
Original data plus 0.4 and rounded	.3625	.602*
Original data plus 0.5 and rounded	.3333	.577
Original data plus 0.6 and rounded	.3333	.577
Original data plus 0.7 and rounded	.2958	.544
Original data plus 0.8 and rounded	.3292	.574
Original data plus 0.9 and rounded	.3833	.619*

average content of 3.2 per cent and an average count length of 1500, the expected variance attributable to analytical procedure is 0.206. This is readily tested against the observed variances, before and after rounding, and the results are shown by the asterisks forming the last column of Table 4. A double asterisk indicates that the excess of observed over expected variance is highly significant, a single asterisk that the excess is suggestive but not conclusive, and a blank that an analytical error alone might account for the observed variation. To the original question the double asterisk thus answers with a firm "yes," the single asterisk says "perhaps," the blank says "no," or, at any rate, "not found." The results after rounding are highly variable; there are 3 double asterisks, 3 single asterisks, and 4 blanks. The occurrence of a blank in the first line and a double asterisk in the second is particularly striking; no evidence of sample variation is found in the original unrounded data, but the operation of rounding makes it appear that observed variation is considerably larger than can be accounted for by analytical error alone. Now the addition of a constant has no effect on dispersion, and it is dispersion with which we are concerned. If we had refrained from rounding, the entries in each column would have been identical, from top to bottom of the table, *as they should be*. Variation in variance, and hence in standard deviation, is generated entirely by rounding.

In this case the apparently innocuous practice of rounding leads to a conclusion exactly opposite to that given by the unrounded data; the rounded values actually mislead us. In other cases the effect of rounding will be merely to throw the data out without seeming to do so. In the tenuous atmosphere in which "broad" or "fundamental" geological problems are discussed, there may often be no practical difference be-

tween rounded and unrounded data—but my own feeling is that this happy circumstance usually arises when the data, whether rounded or not, are no more than window dressing.

The experimental situation which led to the modal analyses we have been discussing is forthright, and the hypothesis being tested could hardly be simpler. With reasonably complicated experimental designs the uncertainty generated by rounding propagates at an alarming rate and in a fashion both devious and complex. Data which have not been butchered by improper rounding are an absolute prerequisite for numerical analysis of even moderate maturity.

Now the effect of all this is bound to be rather puzzling. For most geologists, statistics is still an extracurricular activity, and one of its major charms is that it reinforces our skepticism. In mineralogical and petrographic subjects, and to some extent in structural geology as well, the earliest focus of skepticism is likely to be some field of mensuration. And our first urge is to “. . . ruthlessly discard unnecessary detail beyond the decimal point.” At this stage of development we are concerned chiefly with the interpretation of data and regard the information yielded by tests of precision or reproducibility as offering an objective index of how we are to think about data obtained under less exacting circumstances. We tolerate the “unnecessary” detail only because by using it we can show that in certain situations it may in fact be unnecessary or even misleading. The experimental designs into which we cast our data are still likely to be very simple, so simple that statistics is something of a sheep in wolf's clothing. For the most part we are still making important discriminations by inspection and merely reinforcing them by calculation. In work of this type it is certainly desirable to eliminate unnecessary detail.

As we make the numerical analysis do more and more of our work, the situation changes. The information we formerly preferred to carry in our heads is now removed from the data, where it was once either unnecessary or potentially misleading, only at the peril of rendering the whole analysis invalid.

The point at which we stop recording and start interpreting our measurements is not as clearly defined as we like to suppose, and its location will surely vary with both the data and the observer. As a practical guide it may help to remember that rounding can be done at any time by anyone, that only one person can *unround*, that even he can do so only for so long as he preserves his notebooks, and that unrounded or inadequately rounded data mislead only those willing to be misled. The unwary should not be wasting their time reading technical literature.

The primary purpose of a table presenting new data is to record ob-

servations; if the original observations can not be read directly or reconstructed correctly from the table, they are lost. This is just what happens when the hundredths place is rounded out of conventional silicate analyses, or the tenths place out of modal analyses based on 1000 or more counts. If the loss of the original measurements is a matter of no consequence, it is fair to suppose that there was no real need to make them in the first place.

Finally, I believe there is a strong relation between imagined and realized precision. If a measuring procedure is intrinsically bad, no amount of enthusiasm and labor will help much. But many types of measurement we use in geology are neither intrinsically good nor intrinsically bad; they are sound if we use them properly and unsound if we do not. The prior conviction that such a method is "rough" or "approximate" practically assures that the results will be much worse than that. Whatever may be the case with football players, the good professional naturalist is always an amateur willing to make the old college try. We have seen an example of the damage done by rounding prior to calculation. The man who makes "rough" measurements by an "approximate" method to "determine an order of magnitude" is guilty of rounding prior to observation. The attitude and procedure are sometimes unavoidable, but that is their only recommendation.

I recall dimly that there is always an error of closure in mapping. From brief but disastrous experience I also recall that this error may be very large unless one is willing to fight all the time to keep it small. An index of refraction determination is not likely to be much good in the third place unless the mineralogist who made it did considerable fussing over the fourth. A petrographer overimpressed by a precision error of one per cent is likely to produce modal analyses which do not even report the order of dominance of the major constituents correctly. For this last type of error, which I have encountered frequently and described at length elsewhere (Chayes, 1952, pp. 226-232) there seems to be no completely rational explanation. No doubt it is sometimes due to faulty material or inadequate technique. But that is by no means the whole explanation, for in some cases the equipment was suitable and the procedure—on paper—proper. What seems to have been lacking was the firm conviction that good measurements are worth making. The absence of this conviction—what I have called above rounding prior to observation—is even more wasteful than rounding prior to calculation. A too easy tolerance of the second practice creates a mental set in favor of the first, with the result that we play with numbers instead of working with them or making them work for us. This is not a statistical problem and the statistician usually evades or ignores it, flattering us and clearing

his own skirts by supposing that we think our measurements worth making.

Obviously the psychological fault of rounding before observation should be avoided wherever possible. Refraining entirely from the use of numbers is often preferable to the all too common practice of dressing up our guesses in them. The measurement we are about to make should always be the best of its kind ever made.

Rounding which makes the class interval broader than the unit of measurement—the continuous least count where that is deducible—should never be performed before the data are recorded and the calculations run.

What this comes to is that tables recording original analytical data will often contain considerable “unnecessary detail” to the right of the decimal point. It is much better to be charged with “pseudo-precision” than to be guilty of pseudo-skepticism.

REFERENCES

- CHAYES, F. (1952), The finer-grained calcalkaline granites of New England: *Jour. Geol.*, **60**, 207–254.
- FAIRBAIRN, H. W., et al. (1951), A cooperative investigation of precision and accuracy in chemical, spectrochemical and modal analysis of silicate rocks: *U. S. Geol. Survey, Bull.*, **980**, 71 pp.
- HAMILTON, W. B. (1952), Precision of geological data: *Bull. Geol. Soc. Am.*, **63**, 323–324.

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X-RAY INVESTIGATION OF COLUSITE, GERMANITE AND RENIÉRITE

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ABSTRACT

X-ray powder photographs of colusite, germanite and reniérite show them to be essentially isostructural. They are isometric or pseudo-isometric, some divergences from a truly isometric pattern being shown. Colusite and germanite are isotropic on the polished surface, but reniérite is strongly anisotropic, and also moderately magnetic. The color of reniérite is bronze brown, as contrasted with the grayish pink of germanite. Reniérite in addition shows more variation than germanite from the normal isometric pattern. The accumulated evidence indicates that germanite and reniérite should be considered separate species.

Average values for the cell edges of the three minerals are as follows:

colusite $a_0 = 10.608 \pm \text{\AA}$, germanite $a_0 = 10.58 \pm \text{\AA}$, reniérite $a_0 = 10.58 \pm \text{\AA}$.

Relative intensities of the diffraction lines correspond very closely, with the exception of those corresponding to the following group of spacings:

Form	Intensity		
	<i>colusite</i>	<i>germanite</i>	<i>reniérite</i>
(002)	2	1	$\frac{1}{2}$
(012)	2	$\frac{1}{2}$	$\frac{1}{2}$
(112)	2	2	2

Nearly all of the lines of the powder photograph of each can be indexed satisfactorily, but for all three minerals rather definite lines appear at about $11.6 \pm \text{\AA}$, that cannot be indexed from the assumed values of a_0 .

HISTORICAL

Colusite was first noted as a probable new mineral, and called "bronze enargite" by Murdoch (10) in 1915, in the course of examination of specimens from Butte, Montana, for the Secondary Enrichment Investigation directed by Professor L. C. Graton. The presence of tin was recognized, and imperfect crystals were judged by Professor Palache to be isometric, but the only analysis was unfortunately abortive. The same mineral was later named "colusite" by Reno H. Sales of the Anaconda Copper Mining Company. It was studied in some detail by Landon and Mogilnor (6) and Zachariesen (18), in 1933, and considered to belong to the sphalerite group, with a unit cell edge of $5.30 \pm \text{\AA}$. Later work by Nelson (11), and Berman and Gonyer (1), in 1939 modified some of the earlier conclusions, and showed that the unit cell edge should be doubled, and that the structure was closely related to the tetrahedrite group.

Germanite was first observed from Tsumeb, Southwest Africa, by Schneiderhöhn (13), in 1920, and described as "Rosa Erz," an unknown, new copper iron sulfide. It was described by Pufahl (12) in 1922, with an

analysis, and with recognition of the presence of germanium. Kriesel (4, 5) published further analyses. Thomson (15) in 1924 made a mineralographic study of germanite, and an additional analysis, in which all iron present was attributed to pyrite. [The writer has found a small amount of iron in germanite by a microchemical test on pure material from a polished surface.] De Jong (3) in 1930 attempted to determine the crystal structure by *x*-ray study. He found a value of $5.29 \pm \text{\AA}$ for the cell edge, but suggested that if a different structure were assumed, this value might be doubled.

Reniérite was first noted from the Prince Leopold mine, Kipushi, in the Belgian Congo, by Thoreau (16), in 1928. He observed it as small grains in the sulfide ores, resembling in color, hardness and chemical behavior the "orange bornite" of Murdoch (10). Le graye (7) in 1933 described the mineral more fully, and suggested it might be chalmersite. He determined moderate magnetism, and strong isotropism on the polished surface. His etch reactions with the standard reagents were all negative. Vaes (17) in 1948 redescribed this mineral, and named it reniérite. His analysis showed considerably more iron than germanite, [confirmed by microchemical test on pure material from a polished surface—J.M.] and recorded the presence of germanium, as well as of essential zinc and arsenic. He, too, noted magnetism, sometimes with polarity, and strong anisotropism, with occasional polysynthetic twinning on the polished surface. In addition, he found minute crystals of tetrahedral symmetry with positive forms (111), (*hll*) and (*hhl*) of good quality, and the negative form ($\bar{1}\bar{1}1$) curved and imperfect.

Dr. H. Lambot, at the University of Liège, has published a brief note (19) on reniérite, giving *x*-ray powder data in agreement with mine, and observing also from these that the unit cell edge should be doubled.

A new occurrence of reniérite was brought to the attention of the writer by F. W. Farwell of the American Cyanamid Company. The mineral was discovered by Dr. B. Geier of the Tsumeb Corp., Ltd., as disseminated grains intergrown with galena, pyrite, tennantite, germanite and bornite, in primary ore from the 2390 foot level of the Tsumeb mine, Tsumeb, Southwest Africa. He at first considered it a new mineral and tentatively designated it mineral *X*. However, the *x*-ray powder data show it to belong to the germanite-reniérite group, with physical and chemical properties nearly identical with those of reniérite. Accordingly, the find may be considered as a new locality for reniérite.

Dr. Geier and the Tsumeb Corporation have kindly consented to the incorporation of these new data in this paper, and the author hereby wishes to express his appreciation of this courtesy.

TABLE 1. X-RAY POWDER PHOTOGRAPHS
Average readings in Ångstrom units with $\text{CuK}\alpha$ and $\text{CoK}\alpha$ radiation

Colusite		Germanite		Reniérite		<i>hkl</i>
<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>	
11.88 Å	$\frac{1}{2}$	11.46 Å	$\frac{1}{2}$	11.72 Å	$\frac{1}{2}$	?
11.00 ?	$\frac{1}{2}$	10.13	$\frac{1}{2}$	10.25 ?	$\frac{1}{2}$	001
9.99 ?	$\frac{1}{2}$	8.77 ?	$\frac{1}{2}$	8.96 ?	$\frac{1}{2}$	?
7.46	$\frac{1}{2}$	7.50	1	7.50	1	011
6.80	$\frac{1}{2}$	7.02 ?	$\frac{1}{2}$			?
6.65 ?	$\frac{1}{2}$					?
		6.25 ?	$\frac{1}{2}$			?
6.07	$\frac{1}{2}$	6.11	$\frac{1}{2}$	6.05	$\frac{1}{2}$	111
5.30	2	5.31	1	5.30	$\frac{1}{2}$	002
4.75	2	4.74	$\frac{1}{2}$	4.80	$\frac{1}{2}$	012 ←
4.33	2	4.32	2	4.31	2	112
		3.73	$\frac{1}{2}$	3.75	$\frac{1}{2}$	022
				3.55	$\frac{1}{2}$	003
3.36	2	{ 3.42	$\frac{1}{2}$	3.34	1	?
		{ 3.34	$\frac{1}{2}$			013 ←
3.21	$\frac{1}{2}$					113
3.075	10	3.054	10	3.06	10	222
2.96	$\frac{1}{2}$	2.96	$\frac{1}{2}$	2.96	$\frac{1}{2}$	023
2.83	1	2.83	1	2.82	1	123
2.66	4	2.64	4	2.65	3	004
2.56	$\frac{1}{2}$			2.56	$\frac{1}{2}$	014
2.50	$\frac{1}{2}$	2.49	$\frac{1}{2}$	2.50	$\frac{1}{2}$	033, 114
2.476	$\frac{1}{2}$					?
2.41	$\frac{1}{2}$					133
2.38	$\frac{1}{2}$	2.37	$\frac{1}{2}$	2.386	$\frac{1}{2}$	024
2.32	$\frac{1}{2}$					124
2.26	1	2.255	1	2.255	$\frac{1}{2}$	233
		2.16	$\frac{1}{2}$	2.163	$\frac{1}{2}$	224
2.12	$\frac{1}{2}$			2.13	$\frac{1}{2}$	005
2.08	1	2.083	1	2.075	$\frac{1}{2}$	015, 134 ←
2.018	$\frac{1}{2}$			2.03	$\frac{1}{2}$	115
1.98	$\frac{1}{2}$					025, 234
1.88	8	1.87	8	1.87	8	044
				1.858	$\frac{1}{2}$	?
1.82	$\frac{1}{2}$			1.816	$\frac{1}{2}$	035, 334
		1.791	$\frac{1}{2}$			135
1.773	$\frac{1}{2}$	1.766	$\frac{1}{2}$			006, 244
1.72	$\frac{1}{2}$	1.72	$\frac{1}{2}$	1.722	$\frac{1}{2}$	116, 235
1.60	6	1.596	7	1.595	6	226
1.56	$\frac{1}{2}$	1.562	$\frac{1}{2}$	1.56	$\frac{1}{2}$	136
1.53	1	1.527	1	1.529	1	444
1.495	$\frac{1}{2}$	1.502 ?	$\frac{1}{2}$	1.497	$\frac{1}{2}$	017
		1.479 ?	$\frac{1}{2}$	1.473	$\frac{1}{2}$	117, 155

TABLE 1—(Continued)

Colusite		Germanite		Reniérite		<i>hkl</i>
<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>	<i>d/n</i>	<i>I</i>	
		1.442	$\frac{1}{2}$	$\left\{ \begin{array}{l} 1.444 \\ 1.435 \\ 1.395 \end{array} \right.$	$\left\{ \begin{array}{l} \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \end{array} \right.$	127, 255, 336 ← ? 445, 037, 227 156, 237
1.35	$\frac{1}{2}$	1.343	$\frac{1}{2}$			008
1.323	2	1.323	2	$\left\{ \begin{array}{l} 1.325 \\ 1.317 \end{array} \right.$	$\left\{ \begin{array}{l} 1 \\ 1 \end{array} \right.$	?
1.22	2	1.214	3	1.214	3	266
1.206	$\frac{1}{2}$					238
1.19	1	1.184	1	1.194	$\frac{1}{2}$	048
1.084	3	1.080	4	1.083	2	?
				1.080	1	448
1.023	2			$\left\{ \begin{array}{l} 1.022 \\ 1.020 \end{array} \right.$	$\left\{ \begin{array}{l} 1 \\ 1 \end{array} \right.$	159, 377 ← 666, 2.2.10
		1.019	2	1.016	$\frac{1}{2}$	0.3.10
.9921 ?	$\frac{1}{2}$	1.005	2			
.9411	$\frac{1}{2}$					
.9394	1	.9369	1	.9395	$\frac{1}{2}$	
		.9358	1	.9360	$\frac{1}{2}$	
				.9340	$\frac{1}{2}$	
		.9287 (broad)	1			
.9245 (broad)	$\frac{1}{2}$					
		.9171 (broad)	1			
.8979 (broad)	2					
		.8950 (broad)	3	.8958 (broad)	$\frac{1}{2}$	
.8432 (broad)	$\frac{1}{2}$					
.8396	1					
.8108	$\frac{1}{2}$					
.8074	$\frac{1}{2}$	.8080	$\frac{1}{2}$			
		.8063	$\frac{1}{2}$			

Indexing based on a cubic unit cell with $a_0 = 10.608 \text{ \AA}$ for colusite, $a_0 = 10.585 \text{ \AA}$ for germanite, and $a_0 = 10.583 \text{ \AA}$ for reniérite.

X-RAY STUDY

Colusite, germanite and reniérite are here considered together because they are essentially isostructural, with almost identical spacings and intensities of powder photograph lines. Certain minor variations serve to distinguish them, and in addition germanite and reniérite are characterized by important physical and chemical differences, which warrant their designation as separate species.

The material used in this study is from the type localities. The colusite is from one of the original specimens collected in 1914, from the 1400'

level of the Mountain View Mine, Butte, Montana. The germanite is from Tsumeb in Southwest Africa, and the reniérite from the Prince Leopold Mine, and from the Tsumeb Mine. As observed by earlier workers, these minerals are apparently isometric, hextetrahedral, space groups $\bar{4}3m$, crystals of colusite and reniérite confirming this determination. Germanite has not so far been observed in crystals. As seen in Table 1, spacings and intensities are nearly identical for all three. There are some differences, however, to which attention may be drawn. These are indicated by pointers in the right hand margin of Table 1. It is considered that they are significant. First, there is a small but consistent difference in the value of a_0 between colusite on one hand and germanite and reniérite on the other. Second, the relative intensities in the set of lines (002) (012) (112) for colusite varies distinctly from those

TABLE 2

	Colusite	Germanite	Reniérite
Polished Surface Characteristics			
Color	pale bronze brown	pale grayish pink	orange bronze
Hardness	C	C	C
Optical behavior	isotropic	isotropic	strongly anisotropic dark brown to pale golden brown, or grayish yellow to gray blue [Le graye]
Etch reactions			
HNO ₃	stains brown	stains brown neg. [Schneiderhöhn, Murdoch]	neg. fumes tarnish slightly [Murdoch]
HCl	stains brown	neg.	neg.
KOH	neg.	neg.	neg.
FeCl ₃	neg.	pos. neg. [Schneiderhöhn, Murdoch]	neg.
KCN	scratches develop, solution turns pink	neg.	neg.
HgCl ₂	neg.	neg.	neg.
Physical properties			
Specific Gravity	4.43 ±	4.46 ±	4.3 ±
Cleavage	none	none	none
H	3-4	4	4.5
			Strongly magnetic

ANALYSES

	Colusite		Germanite			Reniérite		
	1	2	3	3a	4	5	6a	6b
Cu	47.99	46.9	42.12	41.57	45.39	41.63	41.18	43.81
Fe	1.09	3.6	7.8	8.39	4.56	13.73	12.80	12.08
Sn	6.71	5.8	—	—	—	—	—	—
V	2.28	—	—	—	—	—	—	—
Te	1.26	0.4	—	—	—	—	—	—
Sb	0.19	0.64	—	—	—	—	—	—
As	9.54	8.40	1.37	—	4.13	0.87	4.95	4.72
S	30.65	29.2	31.27	31.61	30.65	31.51	30.48	31.28
Ge	—	—	10.19	10.96	8.70	7.75	5.46	6.00
Ga	—	—	1.85	1.99	.76	—	0.52	0.55
Zn	—	—	3.95	4.25	2.58	3.53	0.00	0.00
Pb	—	—	0.96	1.03	0.66	—	2.15	0.00
Rem.	—	0.9	—	—	2.12	—	1.96	—
	99.71	95.84	99.49	99.80	99.55	99.02	99.50	99.50

1. Colusite, Butte, Montana, Gonyer in Berman and Gonyer (1).

2. Colusite, Mountain View Mine, Butte, Montana. Anaconda Copper Mining Co. Spectroscopic analysis [J. M.] of colusite from this locality shows important V, undoubtedly accounting for the low summation.

3. Germanite, Tsumeb, Moritz (9). He states that there was an estimated 20% tennantite in the analyzed material, but this is impossible, as the As present, even if all assigned to tennantite, would allow only 6.75% of this mineral. His analysis recalculated to remove this tennantite, is not notably different, as shown in Column 3a above.

4. Germanite, Tsumeb, Kriesel (4). Rem. shows 1.282 Mo, 0.226 SiO₂, with lesser amounts of WO₃, MnO, Ni, Co, Cd, CaO, MgO, C, Au, Ag. This analysis was made on 50 gm. lots, and almost certainly was on contaminated material.

5. Reniérite, Kipushi. Vaes (17).

6a. W. Reiner, Tsumeb, on material 90% pure. Rem. Mo, MgO, CaO, SiO₂.

6b. W. Reiner, Tsumeb, calculated to 99.5% pure, with Pb as galena, Zn as sphalerite.

in the corresponding sets of lines for the other two. Third, a doublet for germanite appears at 3.42 Å and 3.34 Å, of which only one member can be indexed, but for reniérite and colusite definitely only one line appears in each case, under exactly parallel conditions of exposure. Fourth, reniérite and colusite each show a good doublet, 2.135 Å and 2.075 Å, but the line of spacing 2.13 Å is absent in germanite. In the patterns of reniérite and colusite both these lines of the doublet can be indexed. Fifth, reniérite shows well separated doublets at 1.444 Å and 1.435 Å [not indexable], 1.327 Å and 1.317 Å [not indexable], and 1.083 Å and 1.080 Å, [only one of which can be indexed] none of which appear as doublets in colusite or germanite.

PHYSICAL AND CHEMICAL PROPERTIES

The comparative physical and chemical properties of the three minerals are shown in Table 2.

CONCLUSIONS

X-ray powder photographs of germanite and reniérite show conclusively that they are isostructural with colusite, and have practically the same size unit cell. Lines on x-ray powder photographs of all three minerals that cannot be accounted for by any reasonable isometric unit cell, suggest that they are really pseudo-isometric, notwithstanding that colusite and germanite are optically isotropic, at least within range of visual observation. Reniérite, on the other hand, besides having a considerable number of lines in the pattern that cannot be properly indexed on the basis of any reasonable isometric unit cell, is definitely anisotropic, so that it may be considered as certainly pseudo-isometric. In comparison with germanite, the difference in amount of iron, with somewhat less germanium, the difference in color, in magnetism (germanite is entirely nonmagnetic), and the few but important variations in spacings of reflecting planes, as shown in the powder photographs, indicate strongly that reniérite should be considered as an independent species, rather than as ferroan germanite (Fleischer (2)).

My colleague, Professor George Tunell has kindly read the manuscript of this paper and offered valuable suggestions concerning its preparation. The writer wishes to express his appreciation of this assistance.

REFERENCES

1. BERMAN, H., AND GONYER, F. A. (1939), Re-examination of colusite: *Am. Mineral.*, **24**, 377-381.
2. FLEISCHER, M. (1950), Discredited minerals—Reniérite: *Am. Mineral.*, **35**, 136.
3. DE JONG, W. F. (1930), Die Kristallstruktur von Germanit: *Zeit. Kryst.*, **73**, 176-180.
4. KRIESEL, F. W. (1923), Gallium im Germanit von Tsumeb: *Metall u. Erz.*, **20**, 257-59.
5. KRIESEL, F. W. (1924), Über die Analyse des neuen Germanium-Gallium-Mineral "Germanit": *Chem. Zeit.*, **48**, 961.
6. LANDON, R. E., AND MOGILNOR, A. H. (1933), Colusite, a new mineral of the sphalerite group: *Am. Mineral.*, **18**, 528-533.
7. LE GRAYE, M. (1933), Un sulfure double de cuivre et de fer particulier des minerais de cuivre de Katanga: *Bull. de la classe des Sciences de l'Academie Royale*, 5^e series, tome **XIX**, #2.
8. MASSUY, M. (1938), Étude des minerais de cuivre du gisement Prince Leopold (Kipushi) de l'U. M. H. K.: *Annales du service des mines du comité Spécial du Katanga*, tome **XI**.
9. MORITZ, H. (1933), Die sulfideschen Erze der Tsumeb-mine von Aus-Gehenden bis zur XVI Sohle (-460 m): *Jb. Min., B. B.* **67 A**, 118.
10. MURDOCH, J. (1916), Microscopical Determination of the Opaque Minerals. John Wiley & Sons, N. Y.

11. NELSON, R. (1939), Colusite —its occurrence, paragenesis and genetic significance: *Am. Mineral.*, **24**, 369–376.
12. PUFAHL, O. (1922), "Germanit" ein Germanium-mineral und -erz von Tsumeb, Südwestafrika: *Metall u. Erz.*, **19**, 324–325.
13. SCHNEIDERHÖHN, H., Die Erzlagerstätten des Otaviberglandes Deutsch-Südwestafrika: *Metall u. Erz.* 1920, Vol. **17**, #13, 16, 19, 21, 24; Vol. **18**, #10, 11.
14. SCHNEIDERHÖHN, H., AND RAMDOHR, P. (1931), Lehrbuch der Erzmikroskopie II. Berlin.
15. THOMSON, E. (1924), A mineralographic study of germanite: *Univ. Toronto Publ. Geol. Ser., Contrib. Canad. Mineralogy*, **17**, 62–65.
16. THOREAU, G. (1928), Le Gisement Prince Leopold, Kipushi, Katanga: *Mem. de l'Inst. Geol. de l'Université de Louvain*, Vol. **4**, fas. 3, p. 273.
17. VAES, J. F., (1948), Reniérite: *Ann. Soc. Geol. de Belgique*, **72**, 19–32.
18. ZACHARIESEN, W. H. (1933), X-ray examination of colusite: *Am. Mineral.*, **18**, 534–537.
19. LAMBOT, H. (1950), Sur la reniérite: *Ann. Soc. Geol. de Belg.*, **73**, 183–186.

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INVESTIGATION OF THUCHOLITE

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ABSTRACT

The rather unusual mineral thucholite contains about 50 per cent carbon, 25 per cent volatile gases, and 25 per cent ash. The ash commonly consists of thoria, rare earth oxides and uranium oxide. A purified specimen (*i.e.*, freed from contaminating uraninite) of this interesting material from Ontario, Canada, was subjected to a complete chemical analysis of the ash (including a resolution of certain individual rare earths) and two types of analyses on the volatile gas constituents.

The thoria content in this specimen was less than 1 per cent of the ash, in sharp contrast with the higher percentages which have been reported in previous samples. The rare earth fraction contained a singularly high proportion, over 50 per cent, of a single earth, yttrium oxide. The volatile matter consisted primarily of water, carbon dioxide, and methane, with lesser amounts of nitrogen, carbon monoxide, and hydrogen. The composition of such "volatiles" is shown to be a function of the particular technique employed in evolving them.

INTRODUCTION

Thucholite is a mineral of jet-black color, having a hardness of four (on Mohs scale) and a specific gravity of about 1.8.⁴ The chemical composition of the mineral varies widely: it has been reported to contain 40–60 per cent carbon, 20–30 per cent absorbed volatile gases, with the remainder ash.⁵ Rare earth oxides, uranium oxide and thorium oxide compose the larger percentage of the ash; smaller amounts of lead, calcium, and magnesium oxides are probably present. Although reported from several regions^{4,6,7} thucholite has to the present date been found mainly in pegmatite dikes. It occurs in intimate association with the primary minerals uraninite, feldspar and mica and, according to Ellsworth, appears to be as much a primary mineral as any of these. The discovery of thucholite raises several questions which are of interest from both the chemical and the geological standpoints.

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⁴ Ellsworth, Rare-element minerals of Canada, *Canadian Department of Mines, Economic Geology Series*, No. 11, 178–85 (1932).

⁵ Ellsworth, *ibid.*, 266–267.

⁶ Ikawa, *J. Chem. Soc. Jap.*, **58**, 1135–1143 (1937).

⁷ Spence, *Am. Mineral.*, **15**, 495–520 (1930).

TABLE 1. PROXIMATE ANALYSIS OF PARRY SOUND THUCHOLITE

Volatile gases	26.08%
H ₂ O (direct)	12.96
Gas by difference	13.12
Ash	28.06
Fixed carbon	45.86
Total	100.00%

TABLE 2. ULTIMATE ANALYSIS OF ASH

Water soluble	1.60%
PbO	0.20
U ₃ O ₈	5.80
ThO ₂	48.48
(Ce, La, Dy) ₂ O ₃	5.45
(Yt, Er) ₂ O ₃	10.95
Fe ₂ O ₃	1.50
V ₂ O ₅	2.25
MnO	0.02
Al ₂ O ₃	1.45
CaO	0.50
ZrO ₂	0.80
K ₂ O	0.15
Na ₂ O	0.22
P ₂ O ₅	3.21
SiO ₂	14.70
Total	97.28%

TABLE 3. VOLATILE GASES (VOLUME PER CENT)

CO ₂	6.444%
CO	35.827
CH ₄	1.500
H ₂	44.498
N ₂	3.562
A (includes all rare gases)	0.010
S ₂	0.063
Cl ₂	0.033
F ₂	0.167
H ₂ O	7.857
Total	99.961%

Thucholite has never been found in intimate contact with any carbon-containing material, either in the form of limestone or organic matter. Assuming that the mineral has undergone no alteration, one apparently must accept the fact that carbon is a primary constituent of the granite magma. It appears as though the sorbed volatile gases would comprise a fair sample of the gases surrounding the magma at the time of crystallization. If one assumes that carbon is a primary constituent of the mineral, it would seem that the original composition of the neighboring uraninite should correspond to the formula UO_2 . This question of the original composition of uraninite has been discussed by Ellsworth.⁴

No detailed description of thucholite was made until 1928, when H. V. Ellsworth⁸ described the mineral in detail. He investigated the physical and chemical properties and, with the aid of E. S. Shepherd, was able to report on the individual volatile gases sorbed in the mineral. Table 1 lists their results from a proximate analysis of the major constituents of the mineral while Tables 2 and 3 record the detailed results from analyses performed upon the ash and the sorbed gases in the mineral.

TABLE 4. ANALYSIS OF JAPANESE THUCHOLITE

C	30%
SiO_2	20
Volatile constituents	30
Remainder (ThO_2 , $\text{R.E.}_2\text{O}_3$, etc.)	20
Total	100%

Since Ellsworth was unable to find a near source for the carbon, either as limestone or organic material, he concluded that thucholite was a primary mineral and that carbon must be a constituent of the original magma. H. S. Spence,⁷ however, has reported a very significant occurrence of thucholite and a light oil in the same pegmatite (though at no point in intimate contact).

A mineral similar to thucholite bearing the name "carbo-cer" has been reported by Borneman-Starynkevich.⁹ This mineral has approximately the same density as thucholite and upon burning, leaves 25.6% of its weight as ash. A later article by Ikawa⁶ reports the presence of thucholite in a Japanese pegmatite; his analytical data are given in Table 4.

PRELIMINARY TREATMENT AND EXAMINATION

The specimen chosen for analysis was part of a suite of minerals obtained from the Besner Mine, Ontario, Canada, through Ward's Natural

⁸ Ellsworth, *Am. Mineral.*, **13**, 419-439 (1928).

⁹ Borneman-Starynkevich, *Khibina Apatite*, **6**, 114-118, 270-275 (1933).

Science Establishment. Since the specimen had apparently formed in intimate association with uraninite, it was necessary to separate the two minerals. A density determination using a calibrated pycnometer on a portion of the specimen, however, gave a value of 1.86 g/cc. (taking the density of pure thucholite as 1.77 and of uraninite as 9.0, this would indicate that the specimen was 98.8% pure). The uraninite and thucholite were separated by the well known "sink and float" technique using redistilled 1,2-dibromoethane (specific gravity 2.132) as the liquid medium.

A portion of the separated and dried material was examined qualitatively with a Baird grating spectrograph. Some difficulty was experienced with cyanogen bands in the spectra (due to the large amount of carbon present), since many important lines of the rare earths lie in the region heavily covered by these bands. For this reason neither the rare earths, uranium, thorium, nor calcium can be listed as definitely present on the basis of this examination alone, though all of these are to be expected on the basis of previous work. Only the elements magnesium, silicon, aluminum, beryllium, boron, iron, and lead could be established definitely as present, with yttrium, ytterbium, uranium, thorium, erbium, cerium, neodymium, samarium, and thulium uncertain.

ANALYSES OF VOLATILE GASES

Two different techniques were applied in an effort to identify and determine the volatile sorbed gases. The first method employed a vacuum desorption technique at relatively low temperature (*ca.* 300° C.) in which the gases expelled from the heated and evacuated sample were pulled through a weighed water-collection tube and collected. The weight of water and total volume of gas at atmospheric pressure was determined for a given weight of sample. The gas was then analyzed by successive absorption by various reagents, thus yielding the "percentage-by-volume" composition. The unabsorbable residue (largely nitrogen) was examined spectroscopically in a gas-discharge tube for rare gases.

The second method employed a hot-tube (*ca.* 875° C.) technique in which the gases expelled from a strongly-heated sample were swept by a nitrogen stream through a suitable train of weighed absorbers. This procedure resulted in a "percentage-by-weight" analysis for the volatiles.

In view of the high carbon content of thucholite, it is certainly to be expected that the composition of the gases evolved by the two procedures would differ. The first procedure might be expected to yield results most justifiably interpretable as "absorbed gases" while the high-temperature method, is properly labelled an assay of the "volatile matter." The second procedure had the disadvantage of not permitting the examination

of the inert gases for the possible presence of argon, helium, and other inert gases.

A. LOW-TEMPERATURE ANALYSIS OF ABSORBED GASES

Crushed samples of 50 to 120 mg. of thucholite were weighed into platinum micro-combustion boats. The samples were introduced into a Vycor test tube fitted with a ground glass connection to a conventional Toepler pump. A tared Pregl-type micro-absorption tube containing phosphorus pentoxide was located between the sample tube and pump. Samples were evacuated at room temperature to remove small amounts of superficially adsorbed gases and moisture prior to the collection of material and data for each run. During an analysis the sample was heated at 250° to 300° C. (max.) and repeatedly evacuated with the pump until no further measureable volume of gas emission could be detected. The total gases removed were collected over mercury in graduated 10 or 20 ml. tubes and their volumes measured at prevailing temperature and barometer conditions. Dried air was admitted to the P_2O_5 tube, which was then weighed as a measure of the water evolved. The sample was also reweighed at the conclusion of each analysis as a measure of the total percentage of volatile matter by weight.

Despite the fluctuations in experimental conditions between analyses (up to 50° difference in temperature and variations of two to fourteen hours in the total time of evacuation), the concordance of the results which are summarized in Table 5 indicates that data obtained by such a technique are probably as significant as those obtained by the high-temperature procedure.

TABLE 5. THUCHOLITE VOLATILES BY LOW-TEMPERATURE, VACUUM TECHNIQUE

Analysis No.	% by Wt. Volat.	Ml. Gas (STP) per mg. sample	Mg. H_2O per mg. sample
1	26.55%	0.1318	0.150
2	26.30%	0.1333	0.150
3	—	0.1300	0.153
4	26.40%	0.1325	0.151

At the conclusion of each analysis it was noted that a small yellowed area had developed at the head of the P_2O_5 tube and that the mercury surfaces in the Toepler pump and collecting vessel were faintly discolored with black scum. After oxidative dissolution, both materials were examined by suitable selective chemical tests and proved to contain sulfur. It is possible, therefore, that small amounts of either elemental sulfur or hydrogen sulfide were evolved. Chemical analyses on the mineral itself showed 1.13% sulfur and 2.84% phosphorus pentoxide.

While volumes of 8 to 18 ml. of gas were available for the analyses, it was found very convenient to employ the micro gas-analytical techniques evolved by Blacet, Leighton, *et al.*,¹⁰ in conjunction with a horizontal micro gas buret of only 0.083 ml. total capacity. In applying these techniques small glass thimbles are inverted over mercury to serve as the reaction vessels or "gas pipets" while the absorbing reagents are successively introduced to the gas bubble as solid, essentially "dry" beads on small loops of platinum wire. The changed gas volume after each absorption is determined by returning the bubble to the capillary-tube buret. Results are obtained as rapidly and as conveniently as on the macro scale and the accuracy of the microprocedures compares favorably with conventional techniques. Replicate gas analyses could easily be made on the material from a given run when desired.

Table 6 summarizes the analytical data for the volatile gases obtained from four runs. The gas composition appears to be quite uniform under the conditions adopted. The gas sample was lost before analysis #1 could

TABLE 6. COMPOSITION OF VOLATILE GASES FROM LOW-TEMPERATURE, VACUUM PROCEDURE

Constituent	Percentages by Volume from Run:				Av. of 2, 3, & 4
	#1	#2	#3	#4	
CO ₂	20.56	23.16	22.96	23.14	23.09%
O ₂	0.74	1.33	1.42	1.38	1.38%
CO	17.1	17.11	17.22	17.26	17.20%
H ₂	—	19.38	19.19	19.53	19.37%
CH ₄	—	14.96	14.85	14.94	14.92%
inerts	—	24.00	24.36	23.75	24.04%

be completed. The results reported under #2 represent the averaged values from duplicate analyses on this sample. In #3 a check was also made for unsaturated hydrocarbons which were found to be absent, or present to less than 0.2 volume per cent. The unabsorbable residues (inerts) from #2 and #3 were examined qualitatively with a spectroscope at pressures of 0.01 to 0.5 mm. in a discharge tube. Several lines due to mercury (the confining liquid in the previous work) and a few weak argon lines were noted. There was no distinction from a spectrum of reduced air (atmospheric air residue with absorbable gases removed in the same fashion) produced under comparable excitation conditions. The "inert" gases from thucholite may be presumed to consist primarily of

¹⁰ An excellent summary of these techniques and citations of the original references will be found in vol. II of Furman (ed.), "Scott's Standard Methods of Chemical Analysis," pp. 2537-2545, van Nostrand, ed. 2, 1939.

nitrogen with a proportion of argon comparable to that in the atmosphere and containing no *major* proportions of other rare gases.¹¹

B. COMBUSTION-TUBE ASSAY OF VOLATILE MATTER

The apparatus is shown in detail in Fig. 1. About 200 mg. of the sample was ignited in a combustion boat contained in the quartz tube (*E*) at 875° C. (controlled with thermocouple). The atmosphere of purified nitrogen was prepared from tank nitrogen freed of oxygen by passage through an alkaline pyrogallol solution in (*A*) which was backed with sulfuric acid in (*B*). Traces of organic matter were removed by ignition with cupric oxide in tube (*C*) to form carbon dioxide and water, the latter

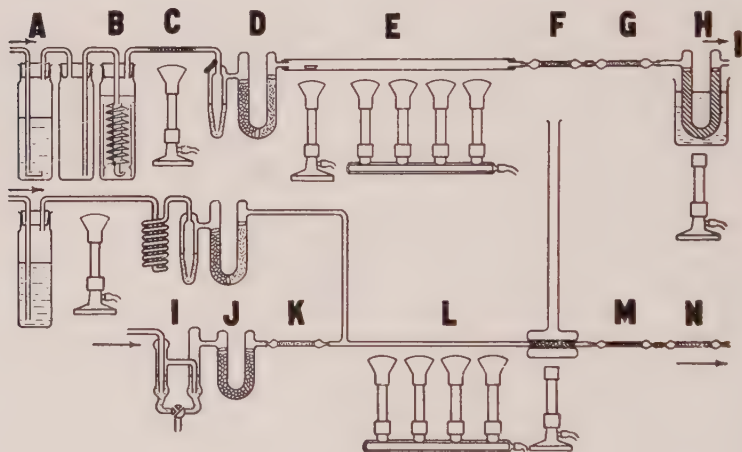


FIG. 1

being removed in the sulfuric acid bubbler and in the Ascarite plus Anhydron absorption tube at (*D*). Water and carbon dioxide evolved from the sample were removed in the tared absorption tubes (*F*) and (*G*) which contained Anhydron and Ascarite, respectively. Any carbon monoxide present was reacted with iodine pentoxide in tube (*H*) at 100° C., to form stoichiometric amounts of carbon dioxide and free iodine. Iodine vapor was removed from the gas stream in a bubbler (*I*) containing 10% potassium iodide solution. The resulting moisture was removed with Anhydron in tube (*J*). The carbon dioxide (equivalent to the carbon monoxide) could then be determined in the tared Ascarite tube (*K*).

At this point, a side-stream of purified oxygen gas was introduced into

¹¹ These results are not necessarily conclusive as regards the absence of small amounts (yet, perhaps, greater than atmospheric) of He, Ne, etc., since the excitation potentials for these elements are much greater than for N₂ or A.

the system. The gas stream which now contained hydrogen, methane, excess nitrogen, and excess oxygen, was passed through a combustion tube (*L*) yielding water from the hydrogen and water plus carbon dioxide from the methane. These products were determined in the tared absorption tubes (*M*) and (*N*) which contained Anhydrone and Ascarite, respectively.

The surface of the ignited samples showed no visible evidence of change, indicating that little oxidation had occurred. The total percentage by weight of volatile matter found by this technique was 21.07% as the average from three runs. The higher value of 26.4% found by the low temperature, vacuum procedure seems definitely to indicate that the removal of volatile matter, even at a temperature lower by 600°, is appreciably more complete with evacuation. Such a comparison of values, however, takes no account of the possible differences in the chemical changes which may have occurred in the residual sample at 275° as compared with 875°. Table 7 records the composition of the evolved gases as determined by the high-temperature evolution technique.

TABLE 7. COMPOSITION OF VOLATILE MATTER BY HIGH-TEMPERATURE TECHNIQUE

Constituent	Percentage by Weight
CO ₂	23.90%
H ₂ O	46.03%
CO	0.34%
CH ₄	15.73%
N ₂ (A, S, etc.)	13.84% (by diff.)

ESTIMATION OF FREE CARBON

Weighed samples of the mineral were heated in platinum crucibles with free access of air to a final temperature of 1000° C. The weight of ash was determined after constant weight had been achieved. Since the percentage by weight of volatiles had been determined, the free carbon was calculated through the relation,

$$\% \text{ free carbon} = 100.00 - \% \text{ volatiles} - \% \text{ ash.}$$

For this purpose, it seemed preferable to use the higher “% volatiles” figure which was based on Procedure “A.” Duplicate determinations of ash gave values of 24.15% and 24.11%, averaging 24.13%. Employing the latter value with 26.42% for the volatiles, one calculates 49.45% for the free carbon.

CHEMICAL ANALYSIS OF ASH

The ash from the preceding determinations was assayed for its constituents by standard chemical procedures. These will not be detailed here,

but the separation techniques employed and the determinative forms used may be followed from a study of the diagrammatic flow-sheet given in Fig. 2. Two samples were analyzed. On one of these, the thorium and ceria were separated from the rare earth oxides by precipitation with iodate after which the rare earths were precipitated from the filtrate as oxalate and ignited to oxides; thorium and ceria were estimated by difference. The total rare earth fraction from the other analysis was later employed for the estimation of its individual rare earth content. On both samples, an R_2O_3 group consisting of U_3O_8 , Fe_2O_3 , Al_2O_3 , and BeO was separated and weighed. The uranium, iron, and aluminum were then isolated and determined individually, but beryllia was estimated only by difference. The possible presence of phosphate may have adversely affected the accuracy of the rare earth and/or the R_2O_3 group analyses.

Data from the analyses of the ash are summarized in Table 8. Particular attention should be drawn to the very low value of thorium plus ceria found; this point will be emphasized later.

TABLE 8. SUMMARY OF CHEMICAL ANALYSIS OF ASH

	Sample 1	Sample 2	Average
SiO_2	15.63%	15.41%	15.52%
PbO	1.05	1.01	1.03
$ThO_2 + CeO_2$	0.54	19.77	19.64
$(R.E.)_2O_3$	18.96		
U_3O_8	53.30	52.88	53.09
Al_2O_3	0.98	0.96	0.97
Fe_2O_3	0.58	0.67	0.63
BeO	0.94	1.46	1.20
CaO	5.33	5.66	5.50
MgO	1.93	1.78	1.86
Total	99.24%	99.60%	99.44%

SPECTROGRAPHIC ANALYSIS OF THE RARE EARTHS

The forty-four milligrams of earth oxides resulting from sample #2 were dissolved in 10 ml. of 6 *N* hydrochloric acid; suitable aliquots of the resulting solution were used for a qualitative and quantitative examination of the earths present. Both the 220 v. direct current arc and spark excitation were used in the qualitative examination of the spectra with the Baird grating spectrograph. Abundant yttrium and ytterbium lines were found; these two elements seemed to be the major constituents. Several lines of lutecium were found, and one line each for erbium and thorium (cyanogen bands again covered many of the available thorium lines).

On the basis of the qualitative indications, standard solutions in 6 *N* hydrochloric acid of yttrium oxide and of ytterbium oxide were prepared. The materials used in these standards had been furnished by the late B. S. Hopkins of the University of Illinois, and consisted of high purity yttria and a 96.33% ytterbia material containing 3.67% of other rare earth oxides, principally lanthanum oxide. Arc excitation at 220 v. D.C. and 8 amperes was employed using the Baird grating spectrograph and with 90 second exposures. Standard and unknown solutions were accurately dispensed into pre-arc'd electrodes. Yttrium lines at 3195.6, 3200.3, and 3203.3 Å were used for the preparation of three yttrium calibration curves. Ytterbium was calibrated on the 3289.4 Å line. The spectra of samples and of calibration standards were recorded consecutively on the same plates. Relative line densities were measured with a spotting microdensitometer and background corrections were applied.

In this manner, values of 2.426, 2.500, and 2.523 mg. per ml. (on 44.0 mg. of sample in 10.0 ml., total volume) of yttrium oxide were found from the three calibration curves. The average, 2.483 mg./ml., gives 56.5% yttrium oxide in the sample. The ytterbium analyses lead to a value of 15.4% ytterbium oxide. These determinations leave a residual 28.1% to be ascribed to erbium oxide, lutecium oxide, thorium oxide, or undetected substances. It should be noted that the previous analyses showed that no more than 0.54% of the ash could be thorium oxide.

DISCUSSION

Goldschmidt and Thomassen¹² have attempted to subdivide the rare earth minerals into classes and subclasses based upon the average content of individual rare earths, Table 9, and this scheme of classification has proved generally satisfactory to the present time. The present variety of thucholite, with a rare earth group consisting almost entirely of ytterbium, would be placed in *Class B, Subclass II, Type b*, a division composed of rare earth minerals containing a relatively high ratio of ytterbium in comparison to other individual rare earths.

It is interesting, however, to recall the work of Marsh¹³ wherein a pitchblende was reported to contain a rare earth group with europium "at least 1000 times more abundant than in a similar mixture of earths from monazite sands, and many times more abundant than in any other known source." In view of the unusual nature of thucholite and pitchblende with respect to this rare earth content, a similarity between the

¹² Goldschmidt and Thomassen, *Videnskapselskapets-Skrifter, I, Matemat. natur. Klasse, Kristiania*, No. 5 (1924).

¹³ Marsh, *J. Chem. Soc.*, 2387-2388 (1929).

TABLE 9. GOLDSCHMIDT-THOMASSEN CLASSIFICATION OF RARE EARTH MINERALS

Classification	Definition	Rare Earth Content (Total = 110)														
		La	Ce	Pr	Nd	61	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tu	Yb	Lu
Class A	<i>Complete Earth Content</i>															
Subclass I.	Cerium earths pre-dominate	9	40	6	24	0	8	0	8	1	6	1?	4	0	2?	1?
Subclass II.	Yttrium earths pre-dominate	4	20	5	20	0	10	0	15	2	10	2?	10	0.1?	7?	2?
Class B	<i>Selective Earth Content</i>															
Subclass I.	Cerium earths pre-dominate															
Type (a)	Monazite type	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Type (b)	Orthite type	12	50	8	24	0	7	0	4	0	ca. 2					
Subclass II.	Yttrium earths pre-dominate															
Type (a)	Ytter—Gadolinite type	9	40	6	24	0	8	0	8	1	6	1?	4	0	2?	1?
Type (b)	Thortveitite type	2	8	4	6	0	6	0	4	2?	4	1?	4	2?	60	8
Type (c)	Xenotime type	1	1	1	2	0	4	0	15	3	18	5?	28	3?	28	6

chemistry of europium and that of ytterbium is of significance. Of most striking importance is the fact that each of these elements may exist as a divalent ion, a property common to only a few of the rare earths. In light of the theory proposed by Ellsworth⁸ that the initial composition of uraninite is UO_2 , it would appear that the reducing condition within the magma at the time of crystallization might well also reduce any europium or ytterbium to the divalent state. Such a reduction might favor the concentration of the rare earth in the original uraninite. The probable origin of some pitchblendes by oxidative alteration of uraninite fits well into this general concept.

In view of the almost complete absence of thorium oxide in the thucholite specimen analyzed, it appears that a new variety of the mineral thucholite may become recognized as further work confirms this one observation. Previous analyses have never resulted in such low percentages of thorium in any thucholite specimen. Ellsworth,⁸ in fact, based the first two letters of the name "thucholite" upon the relatively high content (ca. 50%) of thorium oxide in the ash which he analyzed.

SUMMARY

A relatively complete analysis of a specimen of thucholite has been made. The analysis included the determinations of the oxides in the ash as well as the quantitative spectrographic determinations of certain individual rare earths in the rare earth group.

As a result of the analysis it appears that:

(1) A new species of the mineral thucholite, containing only a trace of thorium, may become recognized.

(2) Another case has been found in which a single rare earth element makes up almost the complete rare earth content of a mineral. It may prove significant that this element, like europium in the similar instance, is capable of existing in the divalent state.

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A METHOD OF EFFECTIVELY INCREASING THE RESOLVING POWER OF A MICROSCOPE TO REVEAL UNSUSPECTED DETAIL IN THIN SECTIONS

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ABSTRACT

The resolving power of an ordinary microscope can be effectively doubled by the use of narrow pencils of highly inclined light. This illumination technique reveals many details in rock thin sections not previously reported in the literature. A mineral with a slightly higher index of refraction than its matrix can be made to exhibit tremendous positive relief. Orthoclase can easily be distinguished from quartz under plane polarized light thus making grain counting procedures much simpler.

Twinning in some feldspars can be observed under plane polarized light. Worm-shaped paths occur in quartz, feldspars and biotite. These are presumed to be paths along which material has migrated through the rocks.

INTRODUCTION

One of the great problems facing petrologists today concerns the mechanism of metasomatism: how do ions or ion complexes move through rocks and minerals where they can react with others to produce new phases? If ions not identical to those already in a structure move through crystals, as well as around them, it is difficult to believe that they do not leave some traces of the paths along which they have traveled. In an attempt to detect such paths an investigation was made of methods of improving the resolving power of the microscope.

The modern petrographic microscope not only has a very well designed optical system but is in most cases well designed from a mechanical point of view. As a matter of fact, it is so well designed that it can be used for most petrographic purposes with very little adjustment or none at all except for minor corrections to ensure centering of the objectives. This has been the situation for so long that the textbooks from which most geologists get their training in optics and optical mineralogy hardly do more than mention the various parts of the microscope, consequently most petrographers do not utilize to the fullest the fine optical system they have at their disposal. To get photomicrographs of the highest quality, the microscope must be so adjusted that the field is adequately illuminated but, of equal importance, the optical and mechanical elements of the system must be so adjusted that the maximum attainable resolving power can be achieved. Wright pointed out, as long ago as 1911, that much greater resolution could be obtained in a petrographic microscope by combining a slightly different method of illumination than is ordinarily used combined with critical focusing of the various optical

elements. Apparently these suggestions have been overlooked. It is the purpose of this paper to recall attention to Wright's pioneering work in this field and to indicate what an immense improvement in resolution can be realized and to illustrate the consequent wealth of information and detail that ensues.

ADJUSTMENT OF THE ILLUMINATION

The image seen in a microscope is produced in quite a different manner from the one observed through a telescope. Light transmitted through a non-self-luminous object is diffracted and forms a diffraction pattern at the rear of the focal plane of the objective of a microscope. The observed image is derived from this diffraction pattern. The details of this theory were first worked out by Abbe and are conveniently summarized by Wright (pp. 42-46, 1911) from whom the following very brief outline has been taken.

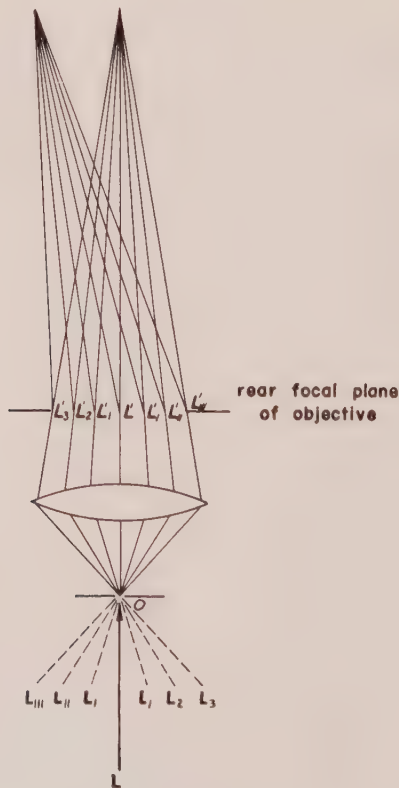


FIG. 1 (After Wright).

A light beam L (Fig. 1) impinging on the object O will be diffracted along the paths indicated by the lines radiating from above the object. If these lines are extended below the object, it would appear as if the object were illuminated from light sources located at L_1, L_2, L_3 , etc. Rays from these apparent light sources are brought to a focus by the objective at its rear focal plane. The actual observed image is formed from these radiant points. These points L_1, L_2, L_3 , etc. are actually produced from the single radiant point L and are therefore coherent¹ and produce waves arriving at the focal plane of the objective at different times, hence produce interference effects.

To produce any interference effects at all, and consequently to attain any resolution, the aperture of the objective must be large enough to allow at least *two* waves (L' and L_1') to reach the focal plane where they can produce one diffraction maximum. If only the central beam L' is transmitted, no diffraction will result and hence no image will appear.

We are interested in determining the minimum distance that two spots must be separated in the object O so that they can be distinguished as two distinct spots in the diffracted image which appears at the rear focal plane of the objective. This minimum distance e is the limit of the resolving power of the system.

In the diffracted image, let us call the distance from the central beam (L') and the first diffracted beam (L_1') e' . This distance is related to the spacing between the two diffracting spots in the object as follows:

$$e' = Ne$$

where N is some whole number.

If L_1' or L_3' were eliminated by some suitable stop, the distance between the central beam and the first diffracted beam would be

$$e' = \frac{Ne}{2}.$$

The same result can be obtained by stopping L_1, L_3 , etc. Since the detail in the image is directly related to the number of radiant points illuminating the object which produce diffraction maxima, elimination of these

¹ In order to produce interference fringes, all the light must come from the same source. It is impossible experimentally to produce interference fringes from two separate light sources. To produce interference effects the path differences of two waves are converted to phase differences (phase difference $= 2\pi/\lambda$ path difference). To do this however we must use perfectly plane polarized monochromatic light with a train of waves infinitely long. In practice, light sources do not produce waves of infinite length. Phase changes occur in any train of waves in a very short period of time (approximately every 10^{-8} seconds) consequently the waves are of finite length, hence interference effects can only be produced experimentally from wave trains emitted by the same source (coherent radiation) that will produce the same changes in all waves at the same time.

rays would halve the detail that could be seen. Conversely, by increasing the number of radiant points the detail observable in the image can be increased. At most, the number of radiant points can be effectively doubled.

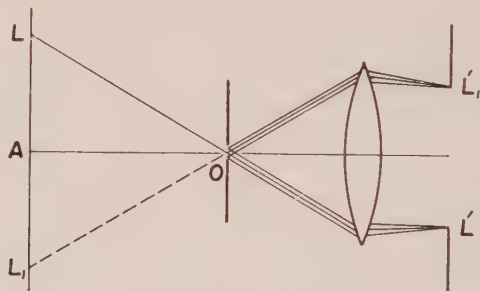


FIG. 2 (After Wright).

Now if only oblique illumination is used (see Fig. 2) with a light source at L , diffraction would occur at the object as if the light came from A ; in addition a symmetrical beam (L') would be produced which appears to come from radiant point L_1 . In other words, by using oblique illumination two radiant points are produced—an apparent one for each “real” one—hence two diffraction maxima will appear in the image for each “real” radiant point. It follows from this that twice as much detail can be seen in the image if oblique illumination is used than if ordinary vertical illumination is employed. This is equivalent to doubling the resolving power of the microscope without altering any of the lens elements of the system.

Not only will more details appear in the image if oblique illumination is used, but slight differences in index of refraction will appear as great relief differences. Advantage is taken of this fact when determining indices of refraction of minerals in a mixture using oblique illumination produced by partially shading the substage mirror with an index finger placed in the beam from the microscope lamp.

ADJUSTING THE CONDENSER

The condenser of a microscope is designed to furnish as wide a cone of incident light as can be possibly accommodated in the objective used. The object is said to be “critically illuminated” where the rays traveling through the condenser are properly focussed on the object. This is accomplished by adjusting the position of the condenser.

The numerical aperture of the condenser should not be larger than that of the objective in use, or else the field will be flooded with light.

The effective numerical aperture of the condenser can be reduced by suitably adjusting the diaphragm built into the condenser housing.

To emphasize the differences in refractive index of the minerals being examined, a narrow beam of sharply focussed light from the condenser should be used. A wide cone of light illuminates the grains from all sides, causing them to appear equally bright hence much of the detail is "washed out." This type of illumination increases the amount of reflected and refracted light which also tends to eliminate detail. Wright pointed out (pp. 88-90, 1911) that almost parallel rays (from the condenser) must be used to detect very slight differences in indices of refraction. By stopping down the diaphragm or by lowering the condenser this condition can be readily satisfied and, as the following photomicrographs will show, extremely small differences in index of refraction between zones in an *individual* grain can give rise to Becke lines which can readily be photographed or observed.

RESULTS

The photomicrographs pictured here were obtained by adjusting the substage diaphragm, critically focussing the condenser, and using oblique illumination transmitted through an ordinary petrographic microscope. The amount of detail seen could sometimes be enhanced by cutting out some of the light as it passed through the microscope tube. This can be conveniently done by inserting one of the accessory plates part way into its slot. Only a microscope and a bellows were used to take the photomicrographs.

To obtain "crisp" photographs, particular care must be taken to get a good focus of the image on the photographic plate. Best focussing results were obtained by removing the plate holder from the bellows and viewing the image through a lens held in the eye like a monocle. The upper lens element from a low power eye piece is ideal for this purpose. This technique gives much better results than the use of a ground glass focussing plate.

SAMPLE PREPARATION

An inspection of the photomicrographs shows that Becke lines delimit the edges of the channels. On raising the focus, the Becke lines move away from the channels indicating that the material within them has a lower index than the bulk of the crystal. This applies to both quartz and feldspars. It is thought that the relief features, the apparent "surface" details and the channels, welts, circular depressions, etc., all arise from compositional differences between individual grains and slight compositional differences within individual minerals.

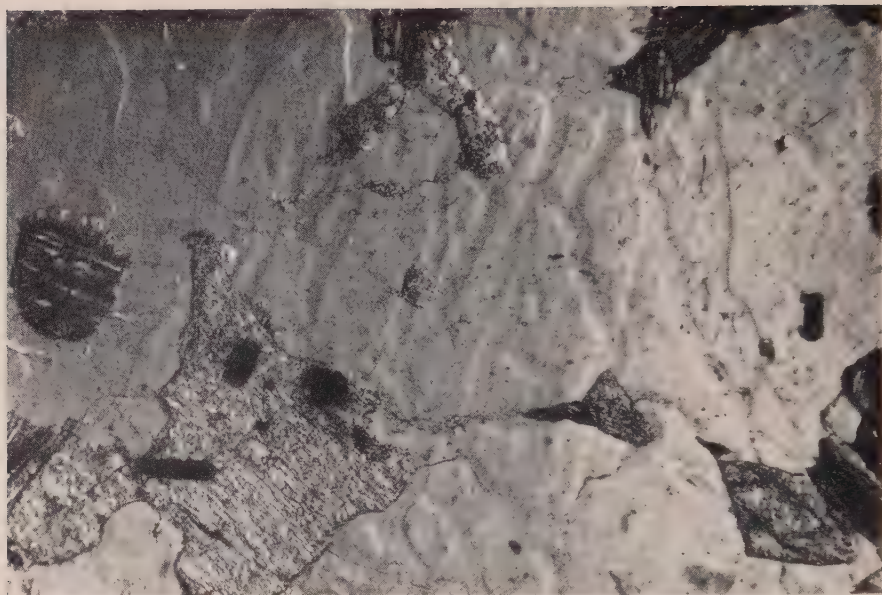


FIG. 3. Highly inclined, plane-polarized light. Mag. 66X. This section contains quartz and highly altered biotite. Note the great differences in relief between the mineral types and details in each. Of principal interest are the numerous "channels" which transect the quartz. These do not appear to follow any crystallographic direction in the quartz. In some cases isolated islands of various shapes remain.

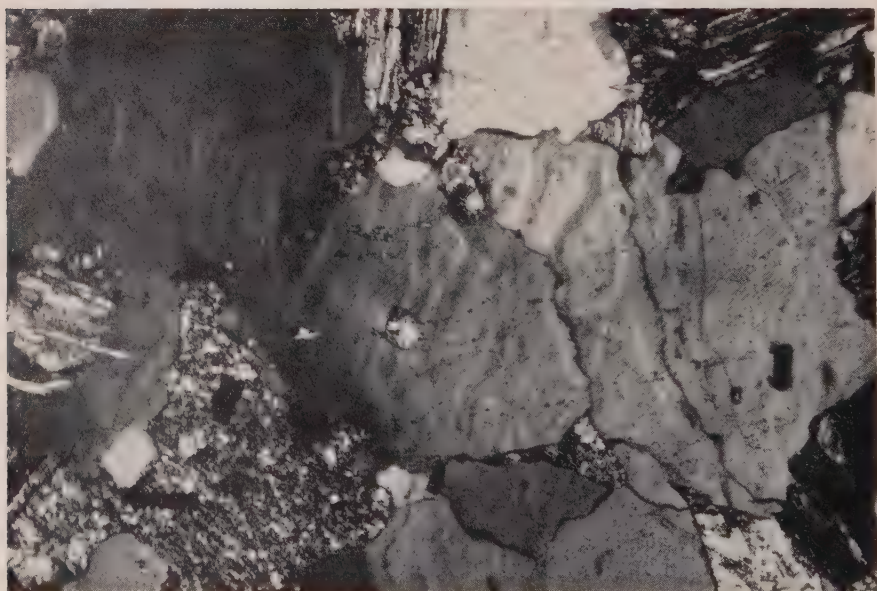


FIG. 4. Same as 3 except under crossed nicols. Note the undulatory extinction in the quartz. It frequently seems to start adjacent to the alteration zones and is thought to be due to a partial collapse of the quartz structure resulting from chemical attack rather than to any physical deformation by outside stresses.

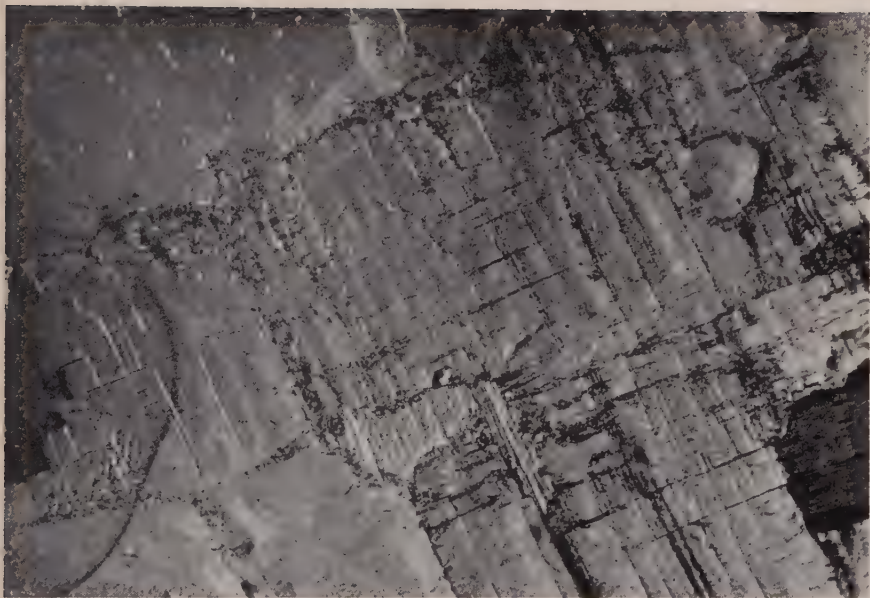


FIG. 5. Highly inclined, plane-polarized light; mag. 66 $\times$. The section contains quartz, oligoclase and muscovite plus an alteration product. The "channels" in quartz follow a sinuous course whereas those in the plagioclase follow the twinning directions as does the alteration. Note that both the albite and pericline twinning lamellae can be clearly seen in *plane polarized light* as relief ridges.

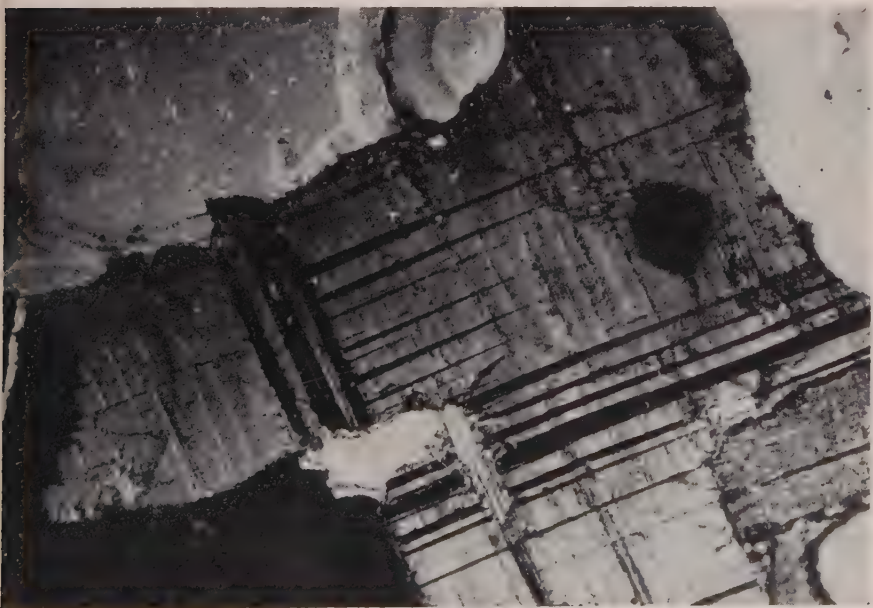


FIG. 6. Crossed nicols of 5. Compare the relief ridges in Fig. 5 with the blacked-out twins.



FIG. 7. Highly inclined, plane-polarized light; mag. 66X. This section contains quartz, biotite, plagioclase and finer-grained alteration product. Note in particular the welts in the quartz and the elliptically-shaped low-relief area. These are apparently related to alteration zones in the quartz which now are filled with a fine-grained muscovite-like product. These circular "depressions" are thought to be cross sections of the sinuous channels seen in this and other thin sections. The channel in the oligoclase appears to be independent of any crystallographic direction.



FIG. 8. Same as 7 except taken under crossed nicols. The channels transect both quartz

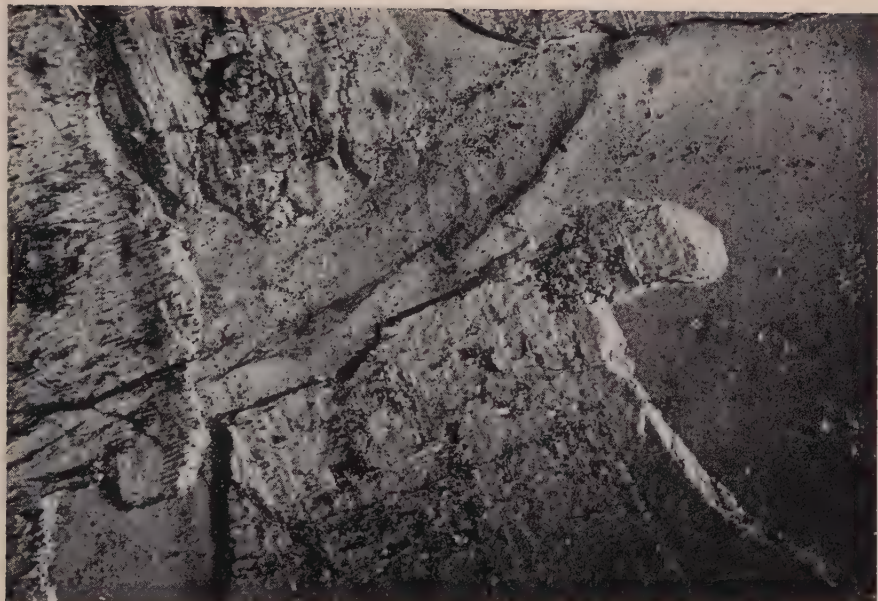


FIG. 9. Highly inclined plane polarized light; mag. 66X. Only quartz, microcline and sericite show in this field of view. This photomicrograph clearly illustrates the great relief differences that can be produced by minerals with relatively small differences in indices of refraction by the use of this technique. A great amount of detail is apparent in both the microcline and quartz. Even the grid twinning of the microcline can be seen under this plane-polarized light. This technique makes it very easy for the petrographer to distinguish by inspection between quartz and orthoclase—a feat not always easy under ordinary circumstances—and hence greatly increase the precision and speed of making grain counts without having to resort to tedious and frequently unsatisfactory staining techniques.

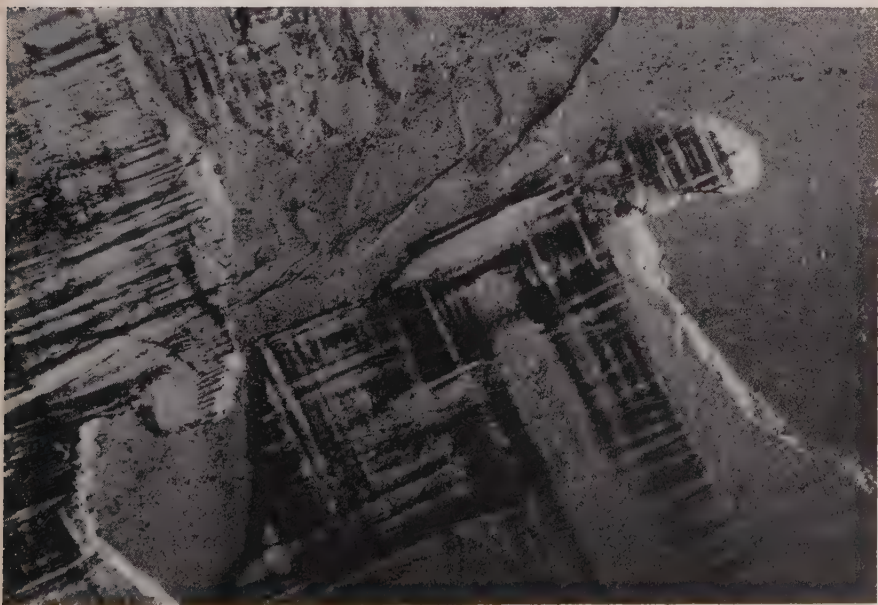


FIG. 10. Same as Fig. 9 except under crossed nicols. The details in the quartz can be seen more clearly than in Fig. 9. These also are thought to be channels but are much more irregular. All transitions between these and the more regularly shaped channels and elliptical zones sometimes can be seen in one thin section.

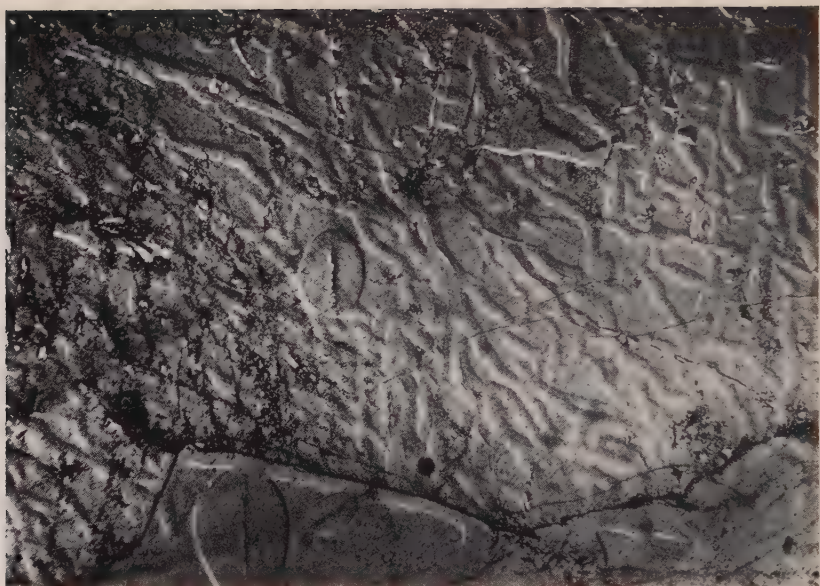


FIG. 11. Plane polarized inclined illumination. Mag. 44X. Notice the swarms of channels through the quartz and oligoclase. The small grains of low relief in the oligoclase are microcline (see the characteristic twinning in Fig. 12). In this section, no relationship exists between channels and crystallographic directions. Note that the channels cross the microcline which is known to be a relatively late mineral to develop in these rocks. The channels can be used as an aid to help solve paragenetic problems.



FIG. 12. Crossed nicols photomicrograph of Fig. 11. Note the circular and oval channels in the quartz. Some of the sericitic alteration develops in the oligoclase at the "mouths" of channels leaving the quartz grains. Potash and water, at the very least, must be introduced in the system to permit the development of the sericite (if the sericite did not grow from colloidal particles). The channels appear to be the paths along which this material has moved.

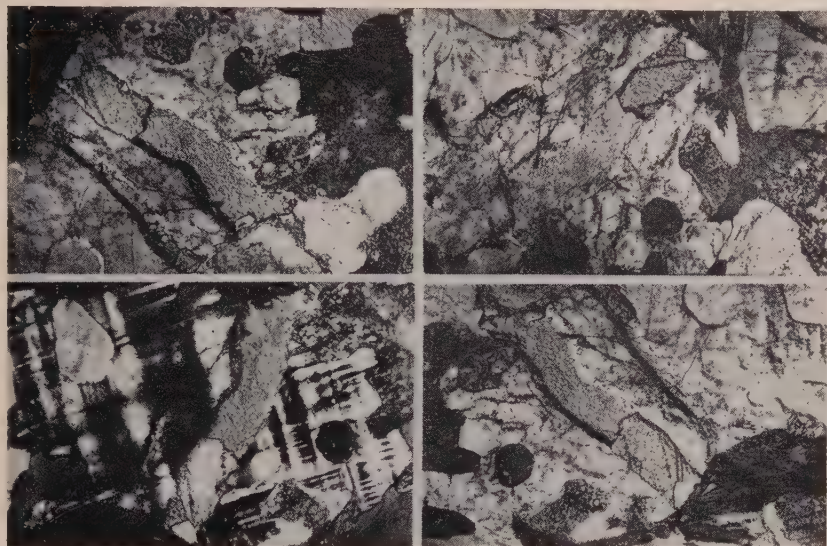


FIG. 13. These photomicrographs illustrate the changes in relief of calcite for different orientations. The stage was rotated 90° after each plane-light photomicrograph was taken (starting at upper left). The calcite is the two rough-surfaced, elongated stringers diagonally across the matrix of microcline. The dark, fibrous material is biotite; the pear-shaped, clear grain is quartz. This and other grains of quartz have higher relief than the microcline.

Note that it is possible to count the color fringes along the edges of the calcite crystals. At least 6 orders can be seen in the original photomicrographs.

From this sequence it is quite clear that the relief features seen in these photomicrographs are neither due to some oddity in the method of preparation of the sections nor to some mounting medium of slightly different properties which might have worked up along grain boundaries before the thin section was covered.

When the channels were first observed, the possibility that they might be due to the method of preparation of the thin sections was investigated. Canada balsam and several synthetic-resins were used as mounting media for different thin sections prepared from the same specimen. In each case the channels remained.

The channels are not due to surface irregularities. Thin sections polished on both sides were made and tested with an optical flat. Although not perfectly flat, the departure therefrom was on an entirely different scale than would be produced by the channels. The Newton-ring patterns did not resemble in any way the photographed patterns of the channels.

From the experiments it can be reasonably concluded that the relief features and the Becke lines which delimit the edges of the channels are truly an optical phenomenon and not due to physical features or surface irregularities on the rock slices. This is further confirmed by the series of photomicrographs showing the relative relief of calcite in microcline for various positions of the microscope stage. The calcite can be made to appear higher, equal to, or lower in relief than the microcline. (See Fig. 13.)

The writer had access to the huge collection of thin sections at the University of Oslo, Norway. Sections prepared for Eskola and Goldschmidt many years ago were examined and they too exhibited the channels. This is further confirmation that the phenomena illustrated in the photomicrographs do not arise from some special method of preparation. After discovering this, all succeeding thin sections were prepared in the ordinary manner—and the channels and other features could still be seen when studied under the illumination technique described herein.

All of the thin sections used for this study were made from rocks from the environs of Kragerø, Norway. The metamorphic rocks in this region include quartzites, amphibolites, hyperites, albitites, a variety of pegmatites and a series of rocks containing sillimanite, andalusite, cordierite, anthophyllite and garnets. These rocks are not unique. The channels and other features shown in the following figures have been observed in rocks from other parts of Norway, from Sweden and England. It is believed, therefore, that features such as these should also occur in similar rocks from other parts of the world.

No attempt will be made in this paper to "explain" the origin and significance of the "channels." A hypothesis accounting for them was presented at the *XIX International Geological Congress in Algiers* (Section XII): a paper offering additional detail is in preparation.

ACKNOWLEDGMENTS

This work was done while the author was a Fulbright research scholar at the University of Oslo, Norway. The work is also part of a U. S. Army Signal Corps research project (No. 33-142-B) devoted, in part, to an attempt to obtain an insight into the mechanism of growth of certain minerals. The author is deeply indebted to the Fulbright program and to the U. S. Army Signal Corps for making this work possible. A deep debt of gratitude is also owed to friends and colleagues in Norway, Sweden and England for their many courtesies and the assistance offered in examining and criticizing the results described herein. I also wish to express gratitude to Dr. F. E. Wright who graciously took time to review this manuscript.

REFERENCE

- WRIGHT, F. E. (1911), *The Methods of Petrographic-Microscopic Research*, Carnegie Institute of Washington, Washington, D. C.

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A SPECTROGRAPHIC METHOD FOR DETERMINING TRACE AMOUNTS OF LEAD IN ZIRCON AND OTHER MINERALS*

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ABSTRACT

Trace amounts of lead in zircon and in some other minerals have been spectrographically determined by the U. S. Geological Survey to provide data in a study of the age of the rocks that contained these particular minerals. Approximately 150 determinations have been made, and one reproducibility test (consisting of 25 observations) has been completed. The material used for the reproducibility test was a silica-base standard containing 30 ppm. lead. The average of the results was 30.4 ppm. lead. On the whole, standard spectrographic procedures were applied, including the split-filter method for calibrating the photographic emulsions.

The method is applicable to samples containing from 0.5 to 1,000 ppm. lead with an estimated accuracy of 6 to 10 per cent. No chemical separations or concentrations are required. The other minerals tested by the method are apatite, sphene, microlite, allanite, and perthite.

INTRODUCTION

The work of E. S. Larsen, Jr., (1952) in using the accessory minerals of granite to determine geologic age is based on ascertaining total radioactivity and total lead. This necessitated a precise and sensitive spectrographic method for the determination of lead in zircon and in other minerals and resulted in the development of a method that is sensitive to as little as 0.5 ppm. lead. To a great extent standard spectrographic procedures have been applied.

Various fluxes, sample weights, types of standards, electrodes, power sources, spectrographic emulsion types, and spectrographs were used in developing the method. The problem revolved around two difficulties, one of which was lead impurities in the chemicals and electrodes (especially in copper electrodes), and the other, the insensitivity of lead in very low concentrations. These problems were solved by systematic elimination and trial-and-error procedures. It was found that, using commercially available special graphite spectroscopic electrodes, an alkaline vapor (sodium carbonate) with type II-O Eastman spectrographic emulsion would record the 2833.1 Å line at a concentration of 0.5 ppm.

The authors wish to express appreciation to their associates of the U. S. Geological Survey, especially to E. S. Larsen, Jr., for providing many of the samples and offering valuable suggestions. This work was done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

* Publication authorized by the Director, U. S. Geological Survey.

PROCEDURE

A method is provided for determining the lead content of zircon samples in the range of 0.5 to 1,000 ppm. lead. It is thought that higher percentages of lead can be determined by applying the same procedure but with changes in transmission and line selection.

The method involves weighing a 12.5 mg. sample, mixing with three parts by weight of sodium carbonate, subjecting the sample and suitable standards to d-c arc excitation in the special graphite spectroscopic electrodes, processing the plate, reading with the densitometer, calibrating the emulsion, and making final calculations.

Apparatus

Excitation source	Multisource d-c arc.
Spectrograph	21-foot Wadsworth-mounted grating, dispersion 5 Å per mm. in the first order.
Intensity control	Neutral filters and split filter (stainless steel on quartz).
Developing equipment	Rocking developing tank, plate washer, and drier.
Electrode cutters	A. Lower electrodes, designed to cut $\frac{1}{4}$ -in. electrodes (outside diameter 0.22 in., inside diameter 0.19 in., depth of crater 0.24 in., depth of shoulder 0.24 in.). National special graphite spectroscopic electrodes. B. Upper electrodes, hemispherical 0.06-in. radius. National special graphite spectroscopic electrodes.
Densitometer	Nonrecording or recording.

Preparation of standards

Standards were prepared by adding solutions of pure lead nitrate to a lead-free base material (silicic acid). The mixtures were evaporated to dryness in platinum crucibles and ground in a boron carbide mortar to pass 100-mesh stainless-steel screen. The material was mixed by passing it through an 80-mesh stainless-steel screen approximately 15 times. The standards were prepared to contain the following concentrations of lead in parts per million: 1, 5, 15, 30, 50, 75, 100, 200, 500, 750, and 1,000. A blank of the base material was similarly processed to determine whether it was contaminated with lead.

A mixture of sodium carbonate and lead-free bismuth, as internal standard, was added to mineral samples, which were then excited in an alkali vapor. This mixture was prepared by adding 0.1 per cent bismuth¹ (or 0.05 per cent bismuth for determining low percentages of lead) to approximately 2 g. lead-free sodium carbonate (Sandell, 1944), and this was processed in the same manner as the standards. The electrodes were loaded with a mixture consisting of 12.5 mg. of the standard and 37.5 mg. of the sodium carbonate and bismuth mixture.

¹ Prepared by dissolving pure bismuth metal in lead-free nitric acid.

The mineral samples were ground in a boron carbide mortar to pass 100-mesh stainless-steel screen. In arcing, the loaded electrode contained 12.5 mg. of sample and 37.5 mg. of the sodium carbonate and bismuth mixture.

ANALYSIS OF UNKNOWN

The samples and suitable standards were placed in the electrode cups (positive) with the aid of a special glass funnel. The electrodes were arced for a period of 120 seconds, and the gap held constant at 6 mm. by manual adjustments. The following multisource conditions and photographic procedures were used:

Capacitance	60 microfarads
Inductance	400 microhenries
Resistance	15 ohms
Initiator	High
Phase	0
Strike	Strike position
Amperes	12 (± 0.5) (d-c arc)
Spectrograph	21-ft Wadsworth-mounted grating
Emulsion	SA-1 (Eastman)
Photographic development	4 minutes at 18° C. ± 0.5 , D-19
Slit	50 microns
Volts	300
Intensity control	Variable
Electrodes	Special graphite spectrographic electrodes

After the plates were processed the transmission values of the following lines were read by applying the nonrecording or recording densitometers:

<i>Bismuth</i> (Å)	<i>Lead</i> (Å)
2938.3	2833.1
2898.0	2823.2
	2802.0
	2663.2
	2614.2

After numerous tests the lead line 2833.1 Å and bismuth line 2898.0 Å were selected for use because these lines approach homologous-pair conditions.

Emulsion calibration

In calibrating the emulsion a two-step method was used. Similar methods, in which a split filter has been substituted for the rotating sector, have been described by Harvey (1950) and Churchill (1944). The split filter (stainless steel on quartz) is an improvement over the step sector because it minimizes or eliminates such well-known disadvantages as stroboscopic, intermittency, and target effects, which are prevalent in the step-sector method.

Calculations

The working curves prepared from the standards served as a check on the standards but were not used in the calculations of final results. The standards indicated reliability by the straightness of the line drawn through the points that were obtained by plotting the relative intensity against the logarithm of the lead concentrations.

By preliminary survey the parts per million of lead were estimated. Standards to bracket the lead content of the samples and the samples themselves were exposed on the same plate. The parts per million of lead were then calculated, employing the x and y coordinates of the relative intensities versus parts per million of lead. This method of calculation has the advantage of using on the same plate a short section of a curve with samples closely bracketed by standards.

TABLE 1. REPRODUCIBILITY DATA ON 30-PPM. LEAD IN SILICA BASE

Observation	Lead ppm.	Difference
1	31	1
2	30	0
3	33	3
4	30	0
5	34	4
6	30	0
7	29	1
8	30	0
9	28	2
10	28	2
11	28	2
12	29	1
13	30	0
14	30	0
15	32	2
16	28	2
17	31	1
18	30	0
19	35	5
20	32	2
21	30	0
22	29	1
23	30	0
24	31	1
25	32	2

No background corrections were necessary, as the background at the lead and bismuth lines was insignificant.

Reproducibility of results

Few data have been collected on the reproducibility of the results obtained by the method. The data on one test, consisting of 25 observations of the 30 ppm. lead standard in silica base, are shown in Table 1. The maximum variation is 5 ppm. lead in 1 observation, and there was no variation in 9 observations. The average of the 25 observations is 30.4 ppm. lead.

Reproducibility of results of lead determinations made at different times is shown in Table 2.

TABLE 2. REPRODUCIBILITY OF RESULTS OF LEAD DETERMINATIONS ON SOME OF THE ZIRCON SAMPLES

Sample no.	Parts per million of lead			
	1st run	2d run	3d run	4th run
Z- 1	86	89		
Z- 3	40	38		
Z- 5	50	49		
Z- 6	33	27	28	33
Z- 7	35			
Z- 8	18			
Z- 9	25	24	23	
Z-11	130	121	127	
Z-40	3			
Z-42	4			

A comparison of lead determinations made by the isotope dilution method, developed by Harrison Brown and his associates (personal communication), and by the method described in this paper gives the following results:

Minerals from Tory Hill, Haliburton area, Ontario	Lead (ppm.)	
	Isotope dilution	Spectrographic
Zircon	461	{ 462 437
Perthite	9.5	5
Sphene	240	245

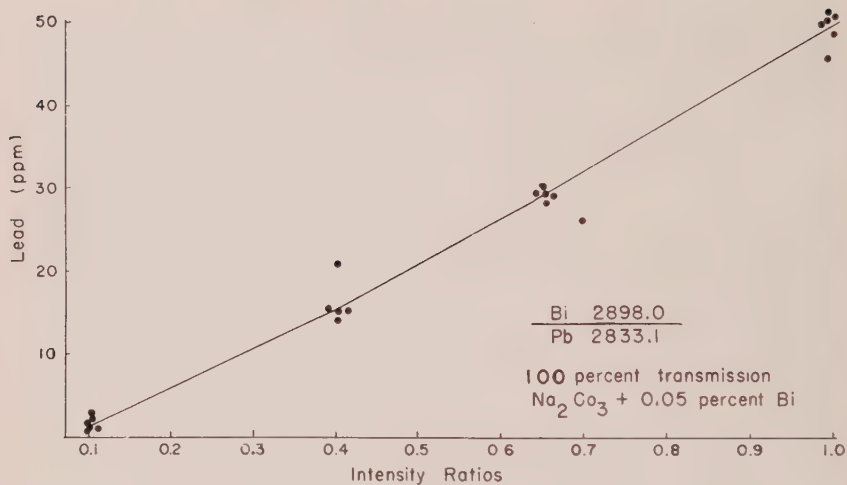


FIG. 1. Working curve for lead in zircon, applied in the range of 1 to 50 ppm. of lead.

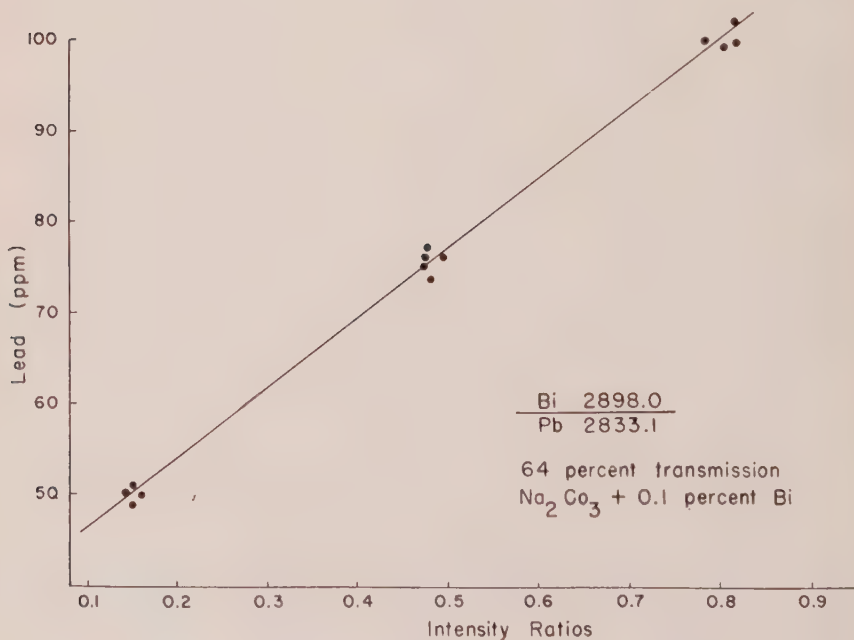


FIG. 2. Working curve for lead in zircon, applied in the range of 50 to 100 ppm. of lead,

It is hoped that microchemical and mass spectrographic techniques will be developed to provide further checks on this method. The precision of the method is estimated to be 6 to 10 per cent.

DISCUSSION

During the course of the analysis it was thought that certain lead results on zircon samples might be high. A microscopic examination of the samples showed foreign particles. Spectroscopic inspection of these particles indicated a high percentage of lead. As the lead in the zircon crystals was of primary interest, it became necessary to treat the samples with dilute aqua regia (1:1) to remove the foreign particles of high lead content that occurred naturally in the samples. This treatment with aqua regia is still in the experimental stage, but it will probably become a part of the standard procedures because it has yielded encouraging results.

Figures 1 and 2 are typical examples of working curves obtained by the described method. Some acceptable curves were also obtained by plotting transmission against lead (in parts per million); this leaves some doubt as to the necessity of an internal standard. Additional tests will be conducted before any conclusions are drawn.

As the chances of contamination are great, the method was designed to reduce the handling of samples to a minimum. It was found that grinding a sample in the agate mortar added a few parts per million of lead to the sample, but grinding a sample in a boron carbide mortar gave no lead contamination. Lead contamination was not detected from the stainless-steel screens, but screening through nylon cloth added a few parts per million of lead.

The d-c arc supplied by the multisource was selected for the tests because of its high degree of sensitivity with the added advantage of simple operation. It is probable that other excitation sources would also produce this sensitivity and could be applied to the trace lead determinations.

REFERENCES

- CHURCHILL, J. R. (1944), Techniques of quantitative spectrographic analysis: *Ind. and Eng. Chemistry, Anal. Ed.*, **16**, 664-665.
- HARVEY, C. E. (1950), Spectrochemical procedures, Glendale, Calif., Applied Research Laboratories, pp. 76-78.
- LARSEN, E. S., JR., KEEVIL, N. B., AND HARRISON, H. C. (1952), Method for determining the age of igneous rocks using the accessory minerals: *Geol. Soc. Am. Bull.*, **63**, 1045-1052.
- SANDELL, E. B. (1944), Colorimetric determination of traces of metals, Interscience Publishers, p. 295.

CRYSTALLOGRAPHIC CONTROL OF REPLACEMENT OF QUARTZ BY FELDSPAR

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ABSTRACT

Quartzite immediately adjacent to the disseminated copper ore body at Bingham, Utah, has been replaced along the quartz grain boundaries by orthoclase. The crystal structure of the quartz has governed the position of the feldspar replacement resulting in partially replaced quartz grains which show a crystallographic outline. Measurements of these faces employing Universal stage technique reveals that the $(10\bar{1}1)$ r or z , and $(2\bar{1}1)$ s or s' , are the largest and most abundant forms. Dissolution of irregularly shaped crystal fragments sometimes produces well-developed definite faces and it is suggested that there might be some similarity in this dissolution phenomenon and replacement along preferred crystallographic directions.

INTRODUCTION

During the course of a study of the disseminated copper deposit at Bingham, Utah, an unusual microscopic feature involving the replacement of quartzite by feldspar was discovered, where the crystal structure of the quartz somewhat governed the place or position where it was replaced by the feldspar. This condition often resulted in a partially replaced quartzite grain which shows crystallographic outline surrounded by the replacing feldspar. Since the original study of the copper deposits

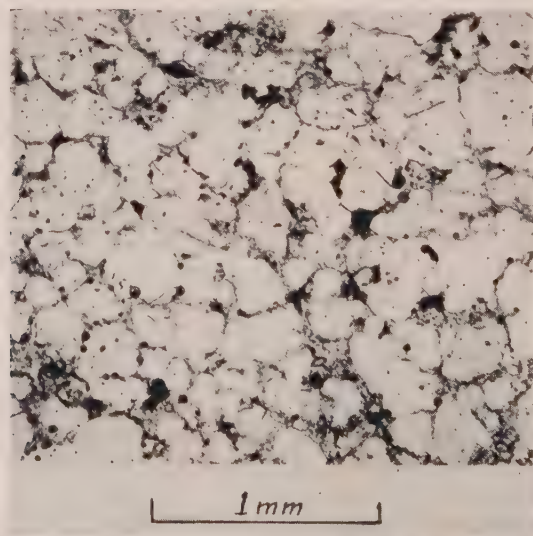


FIG. 1. Photomicrograph of feldspar network in quartzite, uncrossed nicols. Light gray, quartz with interstitial feldspar (turbed dark gray) replacing it along quartzite grain boundaries. Black is introduced pyrite.

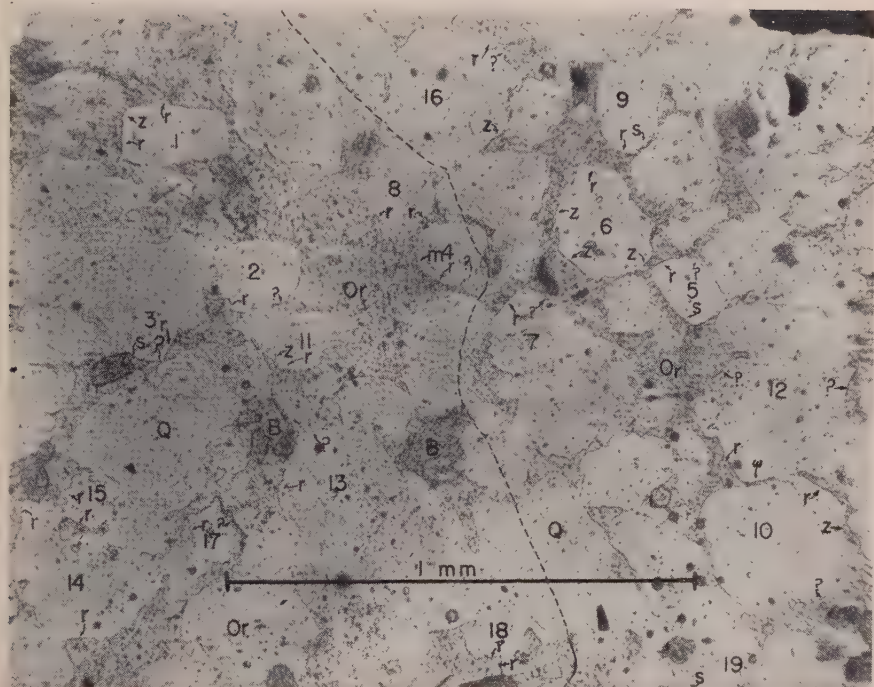


FIG. 2. Photomicrograph of feldspar network, uncrossed nicols. Shows orthoclase (Or) replacing quartzite grains (Q). Small crystals of biotite (B) are contained mainly within orthoclase. Edges of 19 quartz crystals in this field were measured and the crystal faces recorded. The faces questioned are those which could not be recognized as belonging to any of the simpler quartz forms. All of the orthoclase to the right of the dashed line has unit extinction and all of the orthoclase to the left of the line has unit extinction but different from that to the right.

was completed many of these quartz crystal faces have been measured and the results are presented here.

FELDSPAR NETWORK

The term "feldspar network" is used to designate the quartzite which has been replaced by feldspar since the feldspar characteristically has developed along quartzite grain boundaries and often interconnects, simulating a network appearance (Fig. 1). The quartzite containing the feldspar network occurs in areas near the main granite (dark porphyry) within which much of the disseminated ore is found. The replacing feldspar is chiefly orthoclase but plagioclase ($An_{06} - An_{12}$) is often seen. Small euhedral to subhedral biotite crystals are nearly always present in the feldspar, and although they are occasionally seen in contact with the quartz grains, the contacts between the quartz and biotite are always

irregular. The feldspar characteristically replaces along the boundaries of the quartzite grains (See Fig. 2) and often where replacement has progressed to a more complete stage, isolated quartz grains are present and it is mainly on these grains that straight crystallographic boundaries are frequently observed.

METHOD OF MEASUREMENT

The method used was to select a quartz grain having straight edges and to determine the position of the pole of the face with the aid of the universal stage. It was found that many ragged edges of grains would appear straight when tipped on the stage. The c axis of the quartz was always determined and the results of the whole measurement then plotted on transparent paper over a stereographic net. The c axis was then rotated to the center of the net and the poles of the faces rotated correspondingly. In this manner a total of 60 crystals were measured, nineteen of which are

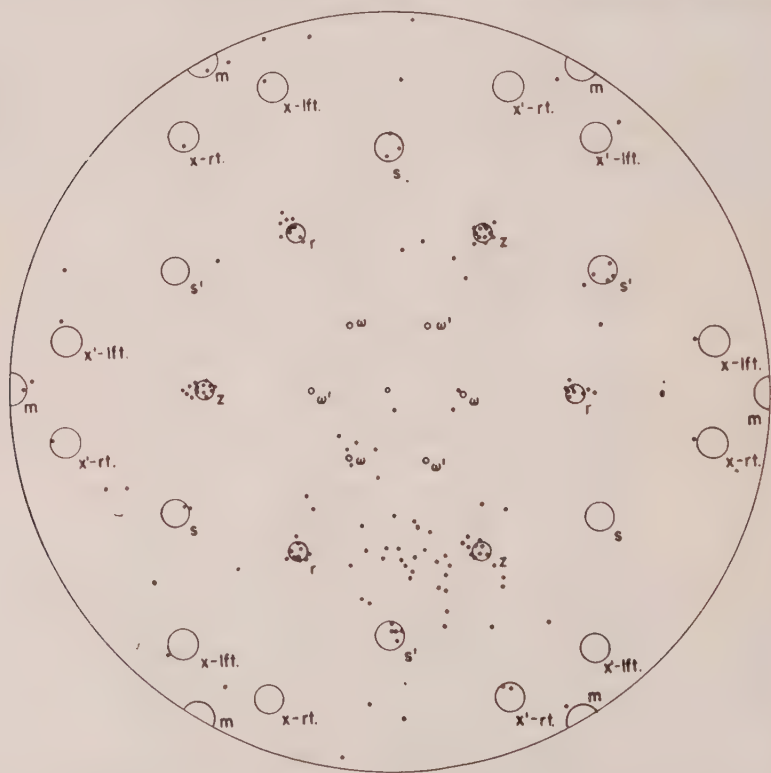


FIG. 3. Stereographic projections of the poles of the measured faces of quartz, c axis vertical. Circles are of 2° radius around the point of the actual pole emergence.

shown in Fig. 2. On each grain selected usually two or more faces were measured.

Using a stereographic net as a base and with the c axis of the quartz vertical, the exact positions of the poles of the common faces of quartz were plotted and the paper on which the measured poles of the faces of the replaced quartzite grain had been plotted was superimposed on it. In a few cases measured poles fell exactly on the poles of actual or possible quartz faces. In most cases, however, the measured poles fell at various positions within 2 to 4° of such poles indicating a moderate error in the measurement, for which it is believed the Becke line between the quartz and feldspar can be held partly responsible. Many measured poles fell in areas quite "remote" from actual common crystal face positions (See Fig. 3) and a chart carrying the actual pole positions of many of the more unusual quartz crystal forms was prepared and the measured points superimposed on it. Only a very few of the measured poles corresponded within a range of expectable error with the unusual forms.

RESULTS OF QUARTZ MEASUREMENTS

On the 60 quartz crystals selected, 182 faces were measured (See Fig. 3) and the following forms were determined:

<i>Form According to Dana</i>	<i>Within 2° Error</i>	<i>Within 4° Error</i>
r and/or z ($10\bar{1}1$)	47	22
s and/or s' ($2\bar{1}\bar{1}1$)	18	1
x and/or x' right and/or left ($51\bar{6}1$)	5	6
m ($10\bar{1}0$)	2	4
ω and/or ω' ($01\bar{1}3$)	1	3
Unknown, does not fall within 4° of any form—65		

It was usually not possible to decide whether a particular face belonged to the form r or to the form z , to the form s' or the form s , since by a 60° rotation of the measured plot a face of the complementary form would have the same position; only an occasional measured plot had enough points falling on actual positions to make such distinctions possible.

The unidentified poles may be the results of large errors or they may represent faces with extremely unusual indices. It was therefore considered impractical to attempt to calculate the indices of these widely spaced poles. If several of the unknown poles had been grouped within the expectable limit of error, an attempt to calculate their indices would have been indicated.

DETAILS OF THE QUARTZ-FELDSPAR CONTACTS

When a quartz-feldspar contact was discovered to be parallel to a quartz crystal face, it was observed nearly always to be a plane and ap-

peared as a sharp line when tipped to a vertical position. Often notches with straight sides indent the quartz, but most of these were too small to measure and it is not known whether the straight sides represent crystallographic directions or not. One notch was found large enough to measure, however, (see lower center of Fig. 2) and both sides were discovered to be rhombohedron faces. The irregular contacts were nearly always fairly smoothly curved in three dimensions. An interesting condition was noted on all unfractured quartzite grains in that the feldspar sought out the intergrain boundaries to replace leaving whole quartz units intact and never replaced "through" a grain leaving two quartz crystals with unit extinction. This could be attributed to accessibility of replacing solutions only along open spaces between grains.

NATURE OF THE FELDSPAR AND BIOTITE

A great majority of the feldspar units were discovered to be quite large, extending with unit extinction for a distance as much as 2 mm. In Fig. 2 only two orientations of feldspar are present. All of the orthoclase on the right side of the dashed line shows unit extinction and this crystal unit extends nearly a full millimeter beyond the border of the illustration. All of the orthoclase on the left side shows unit extinction also. No extremely fine aggregates of feldspar were noted in any of the quartzite sections containing feldspar network. The smallest feldspar anhedral had dimensions around 0.02 mm. This would suggest that when replacing solutions penetrated the rock only a few widely spaced feldspar nuclei were initiated and replacement progressed from these out into the interspaces between quartzite grains. No geometric relationship of the quartz-feldspar boundaries to the crystal structure of the feldspar could be ascertained.

The replacing solutions evidently carried a little material to form biotite and more rarely where a little lime was originally present in the quartzite to make actinolite, and small crystals of these two minerals are nearly always present within the feldspar (See Fig. 2). The orientation of these crystals being at random, they seem to bear no crystallographic relation to the feldspar or the quartz grains with which they are occasionally in contact.

The fact that the solutions carried material other than that to make feldspar perhaps warrants the application of the term *granitization* to the process rather than *feldspathization* since, if the process were more complete a granite or quartz monzonite type rock would result, or if the quartz was entirely replaced, a syenite or monzonite would be the end product.

DISSOLUTION VS. DISPLACEMENT

It is well known that irregular fragments of crystals of many substances when allowed to dissolve will have the irregularities preferentially dis-

solved first and if the fragment is observed during the dissolving process, it will be seen to possess crystal faces, (Buckley 1951). The Bravais (1866) law of crystal growth states that the crystallographic planes having least reticular density will grow fastest thus tending to eliminate these planes as a final crystal face. In the solution of a crystal this law should apply in reverse. Thus, for instance, if the (111) octahedron face is the fastest growing form there should be a tendency for the cube to develop on the crystal. But if the octahedron is the fastest to dissolve the octahedron should be the form resulting (Buckley, 1951). In many cases where alpha quartz crystals have been allowed to grow uninterrupted, the rhombohedron, the plane with lesser reticular density, seems to be a fast growing face resulting in large prism faces and smaller rhombohedral faces.

In the case of this replacement of quartz by feldspar, the rhombohedron is found most frequently, thus suggesting a corollary to the dissolution phenomena.

REFERENCES

1. BRAVAIS, A., *Études Crystallographiques*. Gauthier Villars, Paris (1866).
2. BUCKLEY, H. E., *Crystal Growth*. John Wiley, pp. 304-313 (1951).

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ILVAITE AND PREHNITE IN MICROPEGMATITIC DIORITE, SOUTHEAST PAPUA

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ABSTRACT

Ilvaite and prehnite occur in hydrothermally altered portions of micropegmatitic diorite outcropping in a geologically little known region of Southeastern New Guinea. The ilvaite replaces some of the pyroxenes in the diorite, while prehnite occurs nearby in narrow veinlets cutting through the diorite. Ilmenite is an abundant accessory component. Marked textural features of the micropegmatitic diorite are well-developed micrographic intergrowths between the components of a quartz orthoclase mesostasis, and micrographic intergrowths between pyroxene and ilmenite.

INTRODUCTION

Situated northeast of Milne Bay at the southeastern end of Papua (Fig. 1), micropegmatitic quartz diorite outcrops on the shore platform near Heliego Mission at East Cape, and also forms the basal rock of the shore platform on nearby Meimeiara Island, which is separated from the mainland by a channel two hundred yards wide. Dioritic rocks extend for at least ten miles west of East Cape. Parts have been hydrothermally altered, leading to the production of ilvaite and prehnite.

The area occurs at the southeastern end of the Owen Stanley Ranges, and the outcrops of micropegmatitic quartz diorite evidently represent parts of a small, planated batholith, originally intruded into rocks comprising part of the New Guinea basement complex. All that can be deduced at present of the age of this diorite in the Milne Bay region, is that it is older than the Upper Tertiary rocks of the area, which here consist of limestone and volcanic rocks. Specimens of the volcanic rocks from the Gurney Airfield district (see Fig. 1), are dolerites of variable grain size with well-developed ophitic textures, and altered andesites containing chlorite, clinozoisite, zoisite and albite. The specimens were collected by A. Coulson, in 1945, and were accompanied by field notes.

THE MICROPEGMATITIC DIORITE

The rock is green to black in color and medium-grained. Thin sections from specimens collected at East Cape and on Meimeiara Island, reveal that the rock is generally similar at each locality, but has been subjected to variable degrees of hydrothermal alteration.

The essential minerals in the rock at East Cape are augite and partially altered oligoclase, with a little quartz, rare primary and some secondary hornblende, chlorite, rare biotite as remnants in the chlorite, rare epidote and accessory apatite and iron ores with subsidiary zircon.

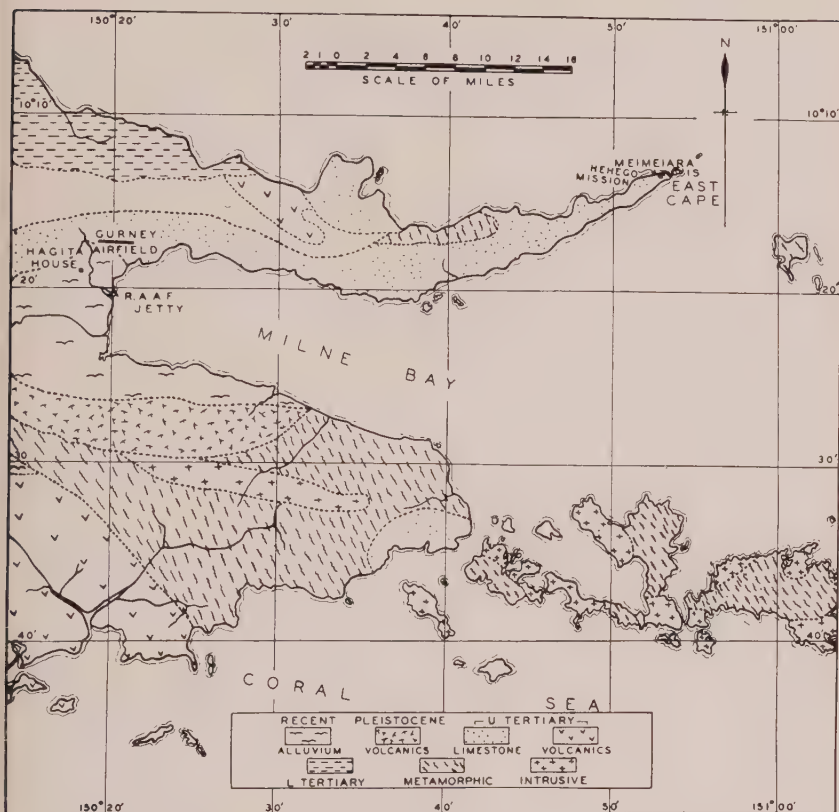


FIG. 1. Geological Sketch Map of the Milne Bay Region, Southeast Papua. Outline based on Australian Army Map (4 miles to 1 inch) of Samarai, First Edition, 1942. Geology from Geological Sketch Map of Eastern New Guinea prepared by Directorate of Research, L.H.Q., Melbourne, December, 1944, from information supplied by J. N. Montgomery, N. Osborne and M. F. Glaessner.

Hatch and Wells (1926, p. 230) state that orthoclase and quartz occur interstitially in diorites and show a tendency towards micrographic intergrowths. Such intergrowths are a characteristic feature of the diorite from East Cape and are particularly well-developed on Meimeia Island. The augite is mainly pale green in color, but some crystals have pale violet, weakly pleochroic, titaniferous cores. Extinction angles are up to 45° . A few pyroxene crystals are markedly fibrous, with a brownish to neutral tint and straight extinction; they carry occasional inclusions along cleavage directions and represent the bronzite variety of enstatite.

On Meimeia Island, the diorite is more altered. It contains abundant ilvaite ($\text{H}_2\text{O} \cdot \text{CaO} \cdot 4\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2$) up to 2.2×1.2 mm. in size, which

is biaxial, intensely pleochroic from dark brown to black in places, shows straight extinction, two distinct cleavages (001 and 010), and in most places is practically opaque in thin section. Where pleochroism can be observed, the ilvaite shows maximum absorption parallel to the more prominent cleavage direction. A polished surface of the rock shows that the dark colored ilvaite takes a relatively good polish and has a reflectivity a little higher than that of the other silicate minerals, but well below that of opaque oxides present. Under the reflecting microscope, the ilvaite shows particularly strong bireflection from a bluish-green to grayish-brown color. It is also strongly anisotropic, polarization colors being reddish-brown and bronze-like. Internal reflections are reddish-brown (cf. Ramdohr, 1950, p. 759).

Parts of the Meimeia Island outcrop contain allanite as a nucleus enclosed by the isomorphous species epidote, which is here typically pistachio-green in color. Occasional hypersthene, not observed in the East Cape outcrop, occurs in the Meimeia Island rock in addition to augite and rare enstatite. Hornblende has been completely altered to chlorite and both the clino- and ortho-pyroxenes are partially chloritized, with flecks of chlorite developed most abundantly along their cleavage directions.

The orthoclase in the micrographic intergrowths has been altered to small opaque masses of kaolinitic material and the associated intergrown quartz is partly strained and biaxial. The oligoclase has not been quite as strongly altered and still retains faint traces of lamellar twinning. It is pale yellowish-green in color from the presence of chlorite along its cleavage planes and from its alteration to fine particles of greenish sericitic matter.

Veinlets of grayish-white prehnite cut through the Meimeia outcrop of dioritic rock. The prehnite shows typical "bow-tie" and radial structures in places, and is accompanied in the veinlets by a little quartz. Where more extensively hydrothermally altered, parts of the diorite are completely altered to a fine-grained zoisite-epidote-chlorite-quartz rock cut by veinlets of quartz and prehnite. Ghost-like outlines of the oligoclase and more clearly defined remnants of the clino- and ortho-pyroxenes testify to the dioritic parentage of the much altered rock. This type of hydrothermal alteration could be attributed to autometamorphic changes brought about by a concentration of volatile constituents in the late magmatic residuum. In view of the occurrence of hydrothermally altered andesites of younger age in the Milne Bay region, however, the diorite may have been partially altered by hydrothermal solutions liberated during Neogene volcanism.

Polished surfaces of the dioritic rocks reveal that ilmenite, the princi-

pal opaque mineral observed, is relatively common and constitutes a few per cent of the rock. The ilmenite occurs mainly in the granular form, but occasionally also as laths. The granules range in size from 0.025 mm. across to 0.40×0.60 mm., and the laths range up to 0.15×0.50 mm.

The ilmenite forms rare micrographic intergrowths with the pyroxene in which it is most commonly set. Evidently its crystallization period occurred principally prior to, but in places overlapped that of the pyroxenes. The constituent parts of the ilmenite in any one of these micrographic intergrowths are all in optical continuity.

The bulk of the ilmenite is structureless in itself, but there are a few small areas where the ilmenite carries closely spaced lamellae of magnetite, thrown down on exsolution along rhombohedral directions in such a manner as to form a marked meshwork structure. In many parts, hematite lamellae are present almost to the exclusion of the magnetite, and in such positions, the magnetite has been largely martitized, possibly from the effects of the hydrothermal solutions that partially altered the dioritic rocks.

The polished surfaces also reveal that the ilmenite and the ilvaite are frequently closely associated. Much of the ilvaite occurs in the areas of pyroxene, but in parts it contains inclusions of ilmenite and evidently formed after the ilmenite. In other parts, however, the ilvaite and the ilmenite occur in micrographic intergrowth, the several parts of the two components in the intergrowths being respectively in optical continuity. Since such intergrowths occur in a rock that has been subjected to hydrothermal alteration, it seems likely that the ilvaite in the intergrowths is a replacement product of the pyroxene, which elsewhere in the rock forms micrographic intergrowths with the ilmenite.

A little limonite, resulting from alteration by weathering of the ilvaite, forms very narrow veinlets cutting through the ilvaite. The ilmenite is principally fresh, but shows occasional alteration to thin rims of leucoxene around crystal edges and narrow veinlets of the same material along cracks.

CHEMICAL COMPOSITION OF THE DIORITE

A chemical analysis of the dioritic rock reveals the constituents listed in Table 1. The rock was analyzed by Mr. G. C. Carlos in the chemical laboratory of the Mineragraphic Investigations Section, Commonwealth Scientific and Industrial Research Organization.

The rock differs chemically from the usual run of diorites in having less alumina, magnesia and alkalies, and more ferrous iron oxide, lime and titania than average diorite (cf. Tyrrell, 1924), most likely as a consequence of the hydrothermal alteration processes. The rock is rich in

TABLE 1

SiO ₂	55.76	
Al ₂ O ₃	10.24	
Fe ₂ O ₃	4.48	
FeO	10.18	
MgO	1.57	Norm.
CaO	9.41	Q—18.72
Na ₂ O	2.27	or— 6.12
K ₂ O	1.01	ab—18.86
H ₂ O (+)	1.80	an—14.73
H ₂ O (-)	0.37	di—26.46
CO ₂	0.02	hy— 0.73
TiO ₂	2.75	mt— 6.50
P ₂ O ₅	0.12	il— 5.32
MnO	0.03	ap— 0.34
Cl ₂	tr.	
SO ₃	tr.	
Total	100.01	

titania for diorites generally, and this finds expression mineralogically in the abundant development of ilmenite. The high normative quartz content is partly a result of the vein quartz accompanying prehnite in veinlets, but is largely due to quartz in the micrographic intergrowths with orthoclase. Some of the FeO and some of the Fe₂O₃ has to be assigned to ilvaite, which also probably contains the small percentage of MnO. The P₂O₅ content is accredited entirely to the numerous, small apatite needles that occur included in both the feldspars and in the pyroxenes.

ACKNOWLEDGMENT

The author is indebted to Dr. A. B. Edwards for critical comments on the mineral determinations.

REFERENCES

- HATCH, F. H., AND WELLS, A. K. (1926), *Textbook of Petrology*, Vol. I. The Petrology of the Igneous Rocks. Allen and Unwin, Ltd., London.
- RAMDOHR, P. (1950), *Die Erzminerale und Ihre Verwachsungen*. Akademie-Verlag, Berlin.
- TYRRELL, G. W. (1924), *Geol. Mag.*, lxi, 19–25.

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A NEW OCCURRENCE OF BARIUM-FELDSPAR AT OTJOSONDU, SOUTH-WEST AFRICA, AND AN X-RAY METHOD FOR DETERMINING THE COMPOSITION OF HYALOPHANE

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ABSTRACT

Four new barium-feldspars Cn_{94} , Cn_{55} , Cn_{50} and Cn_{10} are described. The celsian (Cn_{94}) contains 2.24% Fe_2O_3 (Fe^{3+} probably replacing Al^{3+}) and has refractive indices much higher than material of about the same composition but for iron viz. $\gamma=1.608$, $\beta=1.599$ and $\alpha=1.593$. Similar divergencies occurred in its x-ray diffraction pattern.

Adularia and not sanidine is favoured as the potassium end-member of the series $KAlSi_3O_8-BaAl_2Si_2O_8$. A sudden change in the intensities for similar reflections between the compositions Cn_{37} and Cn_{50} indicates two isomorphous series ($Cn_0-Cn_{40\pm}$ and $Cn_{45\pm}-Cn_{100}$) rather than one (Cn_0-Cn_{100}).

Four variation diagrams based on x-ray diffraction data are offered by means of which the BaO-content of hyalophane ($Cn_0-Cn_{40\pm}$) can be determined to an accuracy of $\pm 5\%$.

INTRODUCTION

In a study of the manganese ores of Otjosondú, South-West Africa, de Villiers (1, p. 95) described two barium-feldspars, hyalophane (Cn_{10}) and celsian (Cn_{94}). Subsequently two feldspars of intermediate composition, Cn_{55} and Cn_{50} , were also found at the same locality.

All these feldspars do not appear to be confined to any particular type of ore. The celsian is associated with a fine-grained vredenburghite-garnet rock, whereas the hyalophane is present as small bodies of irregular shape in a rock composed chiefly of calderite garnet, or as small veinlets traversing the garnet. This celsian and hyalophane were present in amounts large enough to allow their separation from the country rock by mechanical means, and in quantities large enough for detailed chemical analyses. The two intermediate ones (Cn_{55} and Cn_{50}) occur in rocks composed of braunite, garnet and hollandite. They were present in very small quantities and the material eventually submitted for chemical analyses was insufficient for detailed analytical determinations.

The chemical analyses listed are corrected for impurities originally contaminated with the material analyzed. The spectrographic analyses were carried out on material handpicked under the microscope.

CHEMICAL COMPOSITION

(a) *Celsian* (Cn_{94})

Spectrographic analysis

Present: Ba, Al, Si, K, Na, Fe, Ca.

Trace: Mg, Mn.

Absent: Rb, Cs, Li, Sr, B , Be , Ti.

* Published with the consent of the Department of Mines.

TABLE 1

Chemical analysis		Mol. prop.	Molecular composition	
SiO ₂	33.20	0.5528	Celsian (Cn)	94.49
Al ₂ O ₃	25.20	0.2472	Orthoclase (Or)	3.06
Fe ₂ O ₃	2.24	0.0140	Albite (Ab)	1.05
CaO	0.12	0.0030	Anorthite (An)	0.61
Na ₂ O	0.12	0.0019		
K ₂ O	0.52	0.0055	Total	99.16
BaO	38.62	0.2518		
Total	100.04			

Chemical analysis by C. F. J. van der Walt.

A very unusual aspect of the chemical composition of this celsian is the relatively large proportion of Fe^{3+} which probably replaces Al^{3+} . Proof that the Fe^{3+} is contained in the celsian molecule was obtained by grinding handpicked grains of the mineral to a fine powder and boiling the powder in concentrated hydrochloric acid for long intervals over a period of 72 hours. After thorough washing, a spectrographic analysis showed no weakening of the iron lines 3719.9 Å, 3099.9 Å, 3099.97 Å and 3100.3 Å.

The refractive indices of this celsian are also much higher than any recorded in the literature for material of about the same composition, except for the iron. Its x-ray diffraction pattern also shows deviations from that of iron-free celsian (Cn_{89}) from Jakobsberg, Sweden. These deviations support the view that at least a large proportion, if not all the Fe_2O_3 indicated by the chemical analysis, is contained in the celsian molecule. This Fe^{3+} in the molecule evidently causes the abnormalities in its physical properties.

The remaining minor constituents, viz. Na and Ca, are probably not responsible for either the relatively high refractive indices or the divergencies in the angle 2θ for similar reflections, because in most alkali feldspars (which contain these elements in small quantities) their influence is negligible. The spectrographic analysis also indicates that no other elements are present in quantities large enough to have caused these differences.

(b) *Hyalophane* (Cn_{10})

Spectrographic analysis

Present: Si, Al, K, Na, Ba.

Trace: Sr, Mg, Fe, Ca.

Absent: Rb, Cs, Li, B, Be, Mn, Ti.

TABLE 2

Chemical analysis		Mol. prop.	Molecular composition	
SiO ₂	61.17	1.0185	Celsian (Cn)	9.51
Al ₂ O ₃	20.35	0.1996	Orthoclase (Or)	68.15
Na ₂ O	2.92	0.0471	Albite (Ab)	18.28
K ₂ O	11.52	0.1223	Nepheline (Ne)	3.44
BaO	3.89	0.0254		
Total	99.85		Total	99.38

Chemical analysis by C. F. J. van der Walt.

In the calculation of the norm of hyalophane there is a deficiency of silica which results in the formation of a little nepheline. At the same time there is a surplus of 0.47 per cent Al₂O₃. It is, therefore, likely that some Al³⁺ and Ba²⁺ have replaced Si⁴⁺ and Na⁺ and/or K⁺.

The presence of iron (Fe³⁺ or Fe²⁺) in this hyalophane (Cn₁₀) is doubtful because after treatment with acid, in the same way as the celsian, only faint traces of iron could be detected spectrographically.

(c) *The two intermediate feldspars (Cn₅₀ and Cn₅₅)*

Due to the insufficient amounts of available material only the BaO content of these two samples could be determined chemically. They contained 22.5 per cent BaO (Cn₅₅) and 20.4 per cent BaO (Cn₅₀). Spectrographically it was proved that the former (Cn₅₅) contains iron, but the latter was iron-free.

PHYSICAL PROPERTIES

(a) *Optical*

As seen in thin section these barium-feldspars are rarely twinned. They

TABLE 3. OPTICAL PROPERTIES OF S.W.A. BARIUM-FELDSPARS

Sample	Refractive indices			Axial angle	
	α	β	γ	2V (meas.)	2V (cal.)
Cn ₉₄	1.593	1.599	1.608	+85°	+78°30'
Cn ₅₅	1.565	1.572	1.574	-40°	-41°22'
Cn ₅₀	1.555	1.562	1.564	-43°	-41°22'
Cn ₁₀	1.525	1.530	1.532	-62°	-64°36'

TABLE 4. X-RAY DIFFRACTION DATA OF BARIUM-FELDSPARS

No.	Hyalophane (Cn ₁₀)			Celsian, S.W.A. (Cn ₉₄)			Celsian, Sweden (Cn ₈₉)		
	Int.	2 θ (Cu)	d Å	Int.	2 θ (Cu)	d Å	Int.	2 θ (Cu)	d Å
1	3	13.55	6.53	4	13.83	6.39	3	13.98	6.33
2	1	15.09	5.87						
3				2	19.42	4.57	3	19.59	4.53
4	6	21.11	4.01						
5	2	22.61	3.93						
6	8	23.60	3.77	3	23.56	3.77	3	23.75	3.74
7	1	24.69	3.60						
8	5	25.71	3.46	6	25.88	3.44	6	26.06	3.42
9	9	26.98	3.30	7	26.76	3.33	7	26.97	3.30
10	10	27.65	3.22	7	27.52	3.24	7	27.73	3.21
11	8	29.92	2.98	7	29.72	3.00	8	29.94	2.98
12	7	30.80	2.901	4	30.80	2.901	4	31.00	2.882
13	5	32.42	2.759	5	32.43	2.758	5	32.64	2.741
14	8	34.85	2.572	10	34.82	2.574	10	35.06	2.557
15	1	37.01	2.427	3	37.35	2.406	3	37.42	2.401
16	2	38.79	2.319	3	38.85	2.316	3	38.96	2.310
17				2	39.80	2.263	1	39.93	2.256
18	6	41.75	2.162	10	41.65	2.167	10	41.85	2.157
19	1	42.76	2.113	1	42.94	2.104	1	43.02	2.101
20	1	43.98	2.057	1	44.00	2.056	1	44.31	2.042
21	1	45.20	2.004	2	45.46	1.994	2	45.70	1.984
22	1	46.05	1.969	2	46.62	1.946	2	46.68	1.944
23	2	47.30	1.920						
24	1	49.15	1.852	1	49.00	1.857	1	49.41	1.843
25	8	50.78	1.796	5	50.63	1.801	4	51.00	1.789
26	1	54.81	1.673	1	55.71	1.676	1	55.83	1.673
27	2	56.54	1.626	2	56.58	1.625	3	56.72	1.622
28	2	58.78	1.570	2	58.53	1.576	1	58.71	1.571
29	1	60.50	1.529	1	60.87	1.521	1	60.93	1.519
30	7	62.05	1.494	5	63.93	1.455	5	62.02	1.495
31				6	65.30	1.428	5	65.42	1.425
32				2	70.00	1.343	2	70.09	1.342
33				2	71.58	1.317	2	71.72	1.315
34				1	73.50	1.287			

usually exhibit only one good cleavage (001); but in some cases a cleavage parallel to (010) is also developed. Refractive indices were determined according to a single variation method on a Universal stage. The optical properties are listed in Table 3 below. Refractive indices are correct to ± 0.003 at 22°C .

X-ray examination

X-ray diffraction patterns were obtained by using 114.59 mm. diameter cameras and exposing for 2.5 hours to unfiltered Cu-radiation at 35 kV. and 20 mA. The mounting of the films in the cameras, the shrinkage correction factors and the measuring of the films were carried out in the same way as described by the author (2, pp. 946-947). The values of 2θ as listed in Table 4 are considered to be correct to ± 0.03 degrees.

A sample of celsian from Jakobsberg, Sweden (ex. Harvard Univ. Museum No. 10062) containing 36.4 per cent BaO (Cn_{89}) (analysis by C. F. J. van der Walt) was also examined for comparative purposes (see Table 4). This sample is free from iron, its chemical composition is otherwise comparable with that of the S.W.A. celsian, but the x-ray diffraction data on these two minerals vary greatly, no doubt because of the Fe^{3+} which is contained in the unit cell of the South-West African sample.

Table 4 clearly reveals the effect of the Fe^{3+} in the unit cell of the S.W.A. celsian. Similar differences are also encountered when the x-ray diffraction data for the two intermediate samples Cn_{50} (containing no iron) and Cn_{55} (containing 2.9% Fe_2O_3) are compared.

Another striking feature revealed by Table 4 and Plate 1 is that the intensities of reflections from similar crystal planes for hyalophane and celsian are not the same. Table 4 only allows a vertical comparison of intensities visually estimated using an arbitrary scale from zero to 10 for each spectrum. It is clear that the strongest reflections of hyalophane have lost their prominence in the celsian pattern. Fairly weak reflections of hyalophane have become the more prominent ones in the celsian pattern. This alteration of intensities is indicative of some change that has taken place in the crystal structure of barium-feldspars on proceeding from hyalophane (Cn_{10}) in the series KAlSi_3O_8 — $\text{BaAl}_2\text{Si}_2\text{O}_8$ to celsian (Cn_{94}).

Taylor, Darbyshire and Strunz (3, p. 476) suggested that the potassium-rich members of the series are monoclinic, but that celsian is triclinic and only pseudo-monoclinic dimensionally. From this suggestion it would follow that there should be a transition point from KAlSi_3O_8 to $\text{BaAl}_2\text{Si}_2\text{O}_8$, indicating the change in the nature of the dominant atom and separating two isomorphous series from one another. The position of

such a transition point will be determined by the amount of Ba^{2+} that can replace K^+ in hyalophane and at the same time still be bonded into a monoclinic unit. When this critical point is exceeded the structure breaks down to adopt triclinic symmetry which is maintained until all K^+ has been replaced by Ba^{2+} .

NOTES ON THE SERIES KAlSi_3O_8 — $\text{BaAl}_2\text{Si}_2\text{O}_8$

Winchell (4, p. 354) suggested a single isomorphous series between adularia and celsian. He regards hyalophane as a barium-bearing adularia, but is uncertain whether celsian is related to adularia or sanidine, the high temperature form of potash-feldspar. According to Winchell's variation diagram the axial angle of the feldspar Cn_{70} is nearly zero. The low axial angles determined on the two South-West African samples supports the decrease in $2V$ observed for members between Cn_{60} and Cn_{80} .

The variation diagram of Yosimura (6, p. 372) shows notable differences when compared with that of Winchell. Yosimura indicates a break in properties at a point representing hyalophane of about Cn_{40} ($\text{BaO } 16\frac{1}{2}\%$).

A persusal of the literature on the Ba-feldspars (some 45 papers were consulted) reveals such irreconcilable data, that even after verification with new data of South-West African samples, no reliable variation diagram of the optical properties of this series could be compiled.

In order to construct variation diagrams based upon x-ray diffraction it was decided also to investigate a few samples from known localities, bringing the total number of samples examined to fourteen.

THE MATERIAL USED FOR CONSTRUCTING VARIATION DIAGRAMS

(a) *Adularia*

(i) Binnenthal, Valais, Switzerland. (ex. Pretoria Univ. Museum). $2V_\alpha = 62^\circ$. Spectrographic analysis indicates traces of Ca, Ba, Mg and Sr apart from the major constituents Si, Al, K, and Na.

(ii) Gotthard, Switzerland. (ex. Transvaal Museum). $2V_\alpha = 64^\circ$. Apart from the major constituents Si, Al, K, and Na; traces of Mn, Ca, Ba, Sr, Mg and Rb were encountered.

(iii) Mayrhofen, Zillertal, Tyrol. (ex. Transvaal Museum). $2V_\alpha = 63^\circ$. Traces of Ba and Sr were found on the spectrograph in addition to the major components.

The x-ray diffraction patterns of these three adularia samples are identical. The angle 2θ for similar reflections was found to vary only within the limits of experimental error. The average result for these three samples was used in the variation diagrams where it is represented by the letter *a*.

(b) *Sanidine*

(i) Mt. Cumini, Italy. (ex. Transvaal Museum). $2V_\alpha = 14^\circ$. The major constituents are Si, Al, Na, and K with traces of Ba, Sr, Rb and Ca.

(ii) Bolanitos Quarry, Mt. Guagujuata, Mexico. (ex. Transvaal Museum). $2V_\alpha = 40^\circ$. Sodium is not a major constituent but only present as a trace, so also with Ca, Ba and Rb.

(iii) Laacher See, Eifel. (ex. Transvaal Museum). $2V_\alpha = 8^\circ$. Apart from the major constituents Si, Al, K and Na, it also contains traces of Fe, Sr, Ba, Rb and Ca.

The angle 2θ for similar reflections for these three samples of sanidine was also identical within the limits of experimental error. In the construction of the variation diagrams the average value for these three samples was used and is indicated by the letter *b*.

The soda content of five of the above-mentioned samples of adularia and sanidine lies between 0.12 per cent and 2 per cent, and that of the specimen from Mexico was determined to be about 0.12 per cent. This conclusion was reached by taking the three barium-feldspars of known Na-content as standards and deducing by comparison of the intensities of the following sodium lines 3302.3 Å, 3303.0 Å, 4494.3 Å, 4497.7 Å and 4748.0 Å, which represent the sodium content.

(c) Barium-feldspars

(i) Hyalophane, S.W.A. (Cn₁₀). Represented by the letter *c* in the diagrams.

(ii) Hyalophane, Franklin, New Jersey, U.S.A. (ex. Harvard Univ. Museum). Material described by Bauer and Palache (5, p. 174). The chemical analysis of this material is: SiO₂ = 49.51%, Al₂O₃ = 25.48%, K₂O = 9.98%, Na₂O = 3.56% and BaO = 11.47% (Cn₂₈). A spectrographic analysis of the acid purified material reveals a certain amount of Ca, thus indicating that the BaO-content of the chemical analysis may be slightly too high. Its refractive index also indicates a chemical composition of Cn₂₄ rather than Cn₂₈. The specimen is represented by the letter *d* on the graphs.

(iii) Hyalophane, Binnenthal, Valais. (ex. Transvaal Museum). The following is the analysis by C. F. J. v.d. Walt.

TABLE 5. CHEMICAL ANALYSIS OF HYALOPHANE, BINNENTHAL, VALAIS

Chemical analysis		Mol. prop.	Molecular composition	
SiO ₂	51.10	0.8508	Celsian (Cn)	37.28
Al ₂ O ₃	22.10	0.2168	Orthoclase (Or)	47.23
Fe ₂ O ₃	0.40	0.0025	Albite (Ab)	8.45
MgO	0.54	0.0134	Anorthite (An)	3.07
CaO	0.63	0.0112	Nepheline (Ne)	4.28
BaO	15.24	0.0994		
Na ₂ O	2.00	0.0323	Total	100.31
K ₂ O	8.00	0.0849		
Total	100.01			

Represented by the letter *e* on the diagrams.

(iv) Hyalophane, Binnenthal, Valais. (ex. Harvard Univ. Museum No. 10065). The refractive indices of this mineral indicate that its chemical composition is about Cn₃₀. It is represented by the letter *f* on the diagrams.

- (v) Hyalophane, South-West Africa. Cn_{50} , represented by the letter g on the diagrams.
 (vi) Hyalophane, South-West Africa, Cn_{55} , represented by the letter h on the diagrams.
 (vii) Celsian, Jakobsberg, Sweden. (ex. Harvard Univ. Mus. No. 10062). The BaO-content, determined by C. F. J. v.d. Walt, is 36.4 per cent. The spectrographic analysis indicates less than 2 per cent Na_2O . It appears, therefore, that this material is identical to that analyzed by Strandmark (7, p. 298). According to his analysis the material contains 0.22% K_2O and 0.77% Na_2O apart from SiO_2 , Al_2O_3 and BaO. The molecular composition of this feldspar is, therefore, Cn_{89} . It is represented by the letter i on the graphs.
 (viii) Celsian, South-West Africa, represented by the letter j on the graphs.

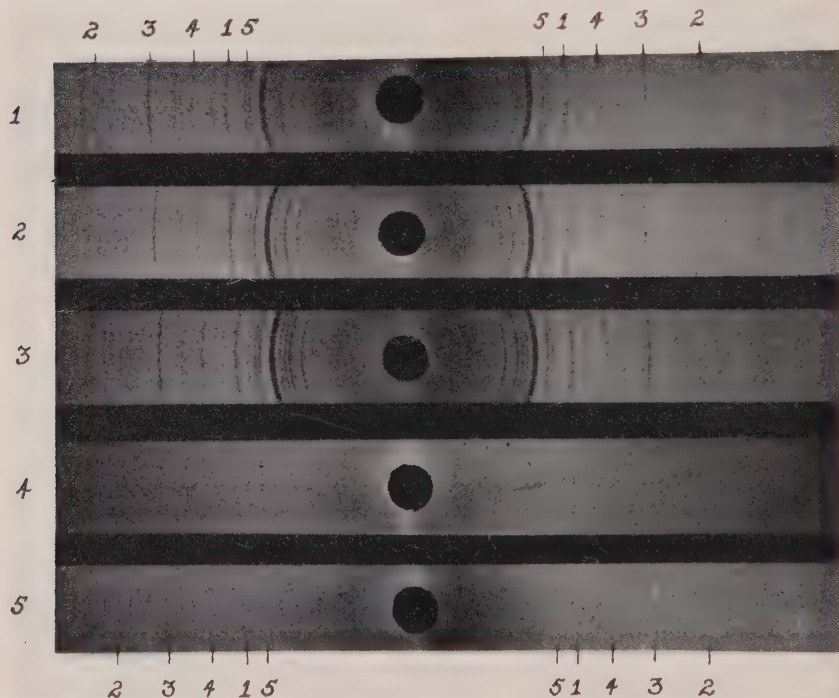


PLATE 1. X RAY DIFFRACTION PATTERNS (CuK) OF: 1. Adularia. 2. Hyalophane (Cn_{10}). 3. Hyalophane (Cn_{37}). 4. Hyalophane (Cn_{50}). 5. Celsian (Cn_{89}).

It seems that the potassium end-members of the series is represented by adularia, the low temperature form of orthoclase rather than by sanidine. This is suggested, in the first place, by the axial angles: $63^\circ \pm 1^\circ$ for almost Ba-free adularia and 62° for hyalophane of composition Cn_{10} , whereas the values for sanidine lie between 8° and 42° .

Moreover, adularia fits much better than does sanidine on the variation curves in Figs. 1 to 4, which are based on x-ray diffraction data.

The intensities of the reflections in the x-ray patterns are the same for adularia and sanidine, as well as for hyalophane of composition Cn_{10} ,

Cn_{24} , Cn_{30} and Cn_{37} . These patterns are characterized by the prominent doublet ($d = 3.29$ and $d = 3.22 \text{ \AA}$) for Cn_{37} . (Lines nos. 9 and 10 in Table 4). This doublet loses its prominence in the patterns of the members of composition Cn_{50} , Cn_{55} , Cn_{89} and Cn_{94} . An examination of Plate 1 discloses numerous other differences in the relative intensities. This sudden change in the intensities for similar reflections indicates that the "transition point" from a monoclinic to a triclinic unit cell is located between the compositions Cn_{37} and Cn_{50} , thus giving rise to two series $Cn_0 - Cn_{40\pm}$ and $Cn_{45\pm} - Cn_{100}$.

Theoretically one would have expected the transition point to be at the composition Cn_{50} , but it clearly occurs displaced slightly towards the potassium end.

Claisse (8, p. 419) has pointed out that in the case of the plagioclase series (having triclinic symmetry from Ab_0 to Ab_{100}) two isomorphous series exist, with a transition point at about Ab_{65} instead of Ab_{50} . In albite the Na^+ ion is surrounded by 6 oxygen atoms, whereas the dominant Ca^{2+} ion of anorthite is probably surrounded by 7 or 8 oxygen atoms, indicating that albite would more easily replace anorthite than vice versa, since the Na^+ ion would find its 6 oxygen atoms in the anorthite

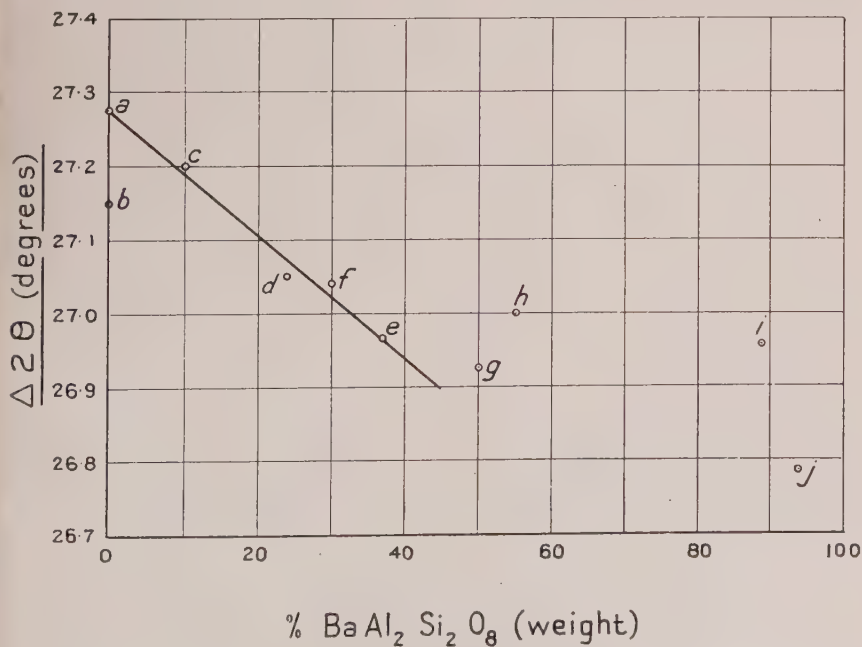


FIG. 1. Graphical representation of the variation of $\Delta 2\theta$ for lines 2-1 with the variation in the chemical composition of hyalophane.

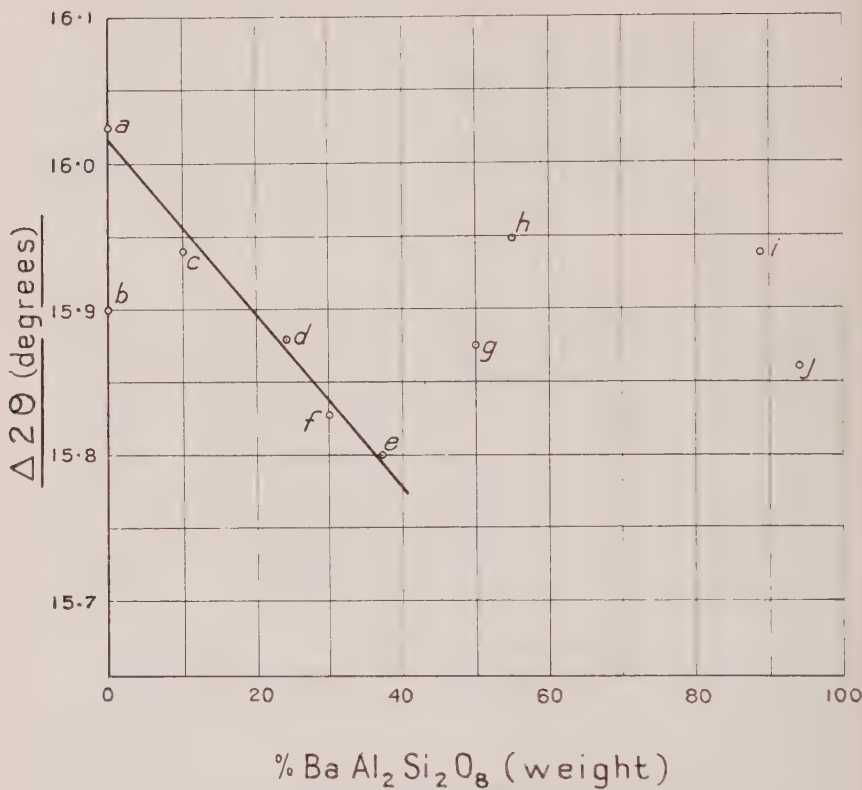


FIG. 2. Graphical representation of the variation of $\Delta 2\theta$ for lines 3-1 with the variation in the chemical composition of hyalophane.

structure more easily than the Ca^{2+} ion could find 7 or 8 in the albite structure.

Taylor, Darbyshire and Strunz (3, p. 477) say that the oxygen atom arrangement is probably substantially the same in all potassium-barium feldspars, although small differences may cause the transition point to be about Cn_{40-45} instead of Cn_{50} .

When the two series $\text{NaAlSi}_3\text{O}_8$ - $\text{CaAl}_2\text{SiO}_8$ and KAlSi_3O_8 - $\text{BaAl}_2\text{Si}_2\text{O}_8$ are compared in general, the first and most obvious resemblance is the similarity of the replacement. In both cases the smaller univalent ion ($\text{K}^+ = 1.33 \text{ \AA}$, $\text{Na}^+ = 0.98 \text{ \AA}$) is replaced by the larger divalent ion ($\text{Ba}^{2+} = 1.43$, $\text{Ca}^{2+} = 1.06 \text{ \AA}$) accompanied by an equal replacement of Si^{4+} by Al^{3+} . From a geometrical viewpoint it can therefore be expected that similar changes in the environment of the dominant cation will take place in both series when the nature of the dominant cation changes.

Direct comparison of the change in the environmental condition of the two series at the transition point is however impossible, as in the case of the Ba-feldspars the transition point also denotes a change in crystal symmetry from monoclinic to triclinic whereas in the plagioclases the triclinic symmetry is maintained throughout the entire series.

AN X-RAY METHOD FOR DETERMINING THE COMPOSITION OF HYALOPHANE

According to Taylor, Darbyshire and Strunz (3, p. 472) the unit cells of barium-feldspars ranging in composition from Cn_{10} to Cn_{37} have approximately the same dimensions. As the physical properties of solid solutions vary with their composition, a study of this series was undertaken by *x*-ray diffraction as a basis of future identification in view of the difficulties experienced by using optical and other methods for this purpose.

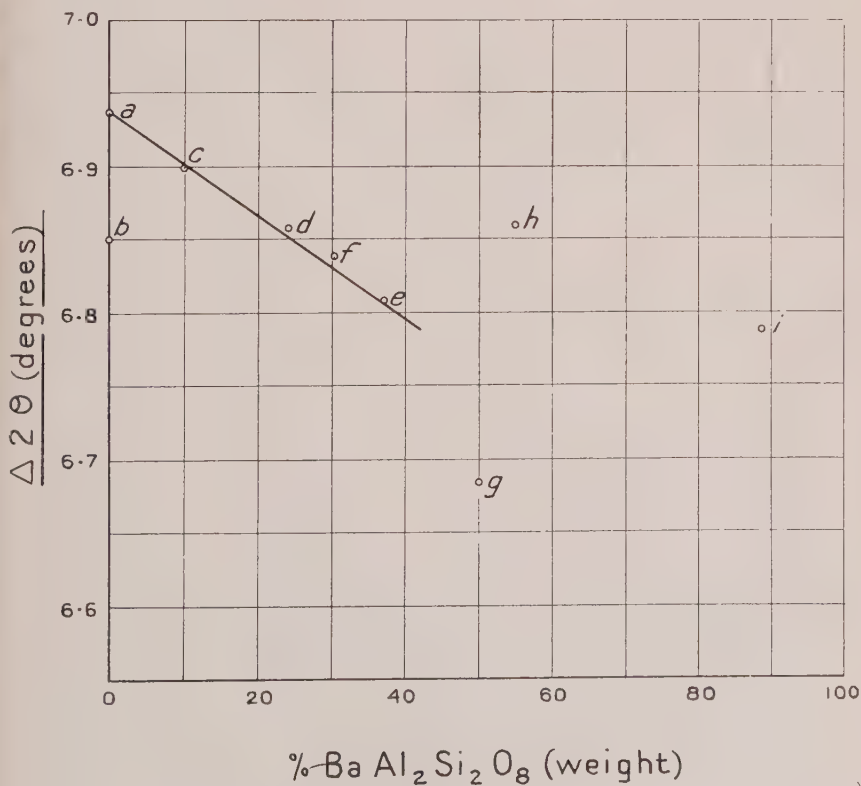


FIG. 3. Graphical representation of the variation of $\Delta 2\theta$ for lines 4-1 with the variation in the chemical composition of hyalophane.

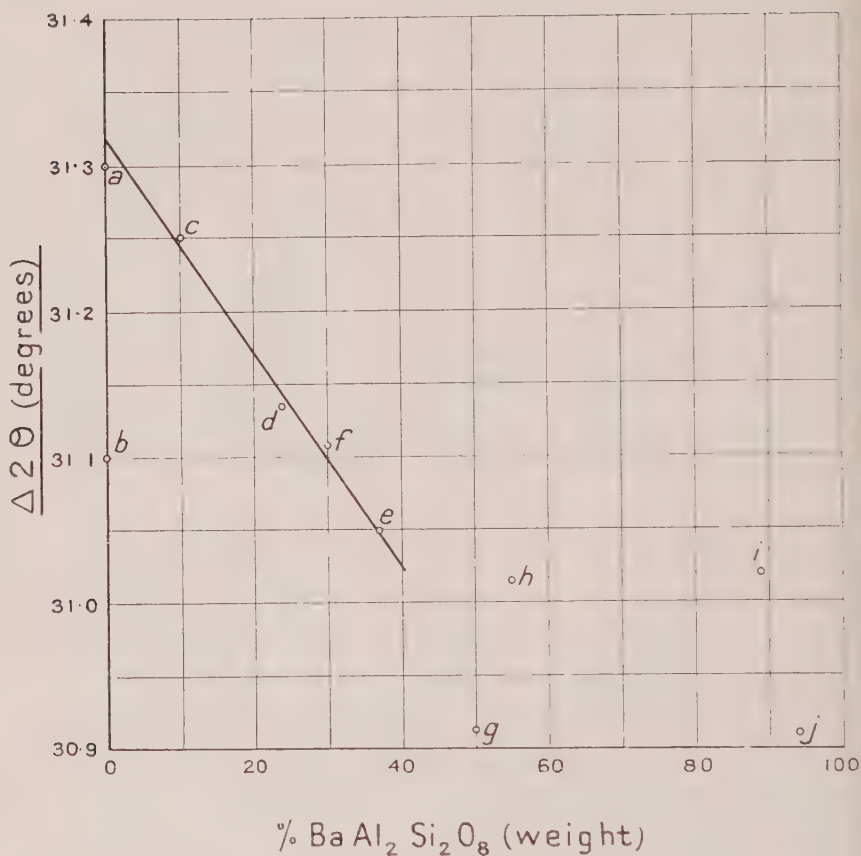


FIGURE 4. Graphical representation of the variation of $\Delta 2\theta$ for lines 5-2 with the variation in the chemical composition of hyalophane.

In any case, there are insufficient representatives known in the range Cn_{50} to Cn_{100} to construct a variation diagram for this second series. Nevertheless, the relevant properties of the few known examples of this composition have also been plotted on the diagrams (Figs. 1 to 4), in order to illustrate clearly the transition point as well as the effect of the replacement by Fe^{3+} of Al^{3+} and possibly of other cations.

In the diffraction patterns of hyalophane of composition ranging from Cn_0 to Cn_{37} it was found that for a given pair of lines the shift was in opposite directions. Because of this complementary shifting of lines due to a change in composition it was found that the differences between the distances of a given pair of lines is a more sensitive method than the differences in the actual distances of each line for different samples.

The data for adularia (a) and sanidine (b) as plotted on all the diagrams

indicate the differences between them and also show that adularia and not sanidine is to be regarded as the potassium end-member.

For the construction of the variation diagrams the lines marked 1, 2, 3, 4 and 5 on Plate 1 were selected as they are relatively prominent, sharply defined and were found to have shifted more than the others. The positions of these five lines are as follows for hyalophane (Cn_{10}) in Table 4.

Line no.	Line no. in Table 4	d A. (for Cn_{10})
1	14	2.574
2	30	1.496
3	25	1.798
4	18	2.163
5	12	2.903

The following four variation diagrams will suffice for purposes of identification.

Precision

The values of 2θ are correct to 0.03 degrees. Therefore, the maximum error of $\Delta 2\theta$ could be 0.06 degrees. Hence, each diagram represents the $BaAl_2Si_2O_8$ -content accurately to within 8 per cent. By using three or more of the diagrams accuracy should be ± 5 per cent $BaAl_2Si_2O_8$, corresponding to a BaO-content of ± 2 per cent.

ACKNOWLEDGMENTS

The author is much indebted to Prof. Clifford Frondel, Professor of Mineralogy, Harvard University, for supplying three samples which have assisted greatly in the compilation of the diagrams.

REFERENCES

1. DE VILLIERS, J. E., The manganese ores of Otjosondou, S.W.A.: *Trans. Geol. Soc. S. A.*, **54**, 89-99 (1951).
2. VERMAAS, F. H. S., Manganese-iron garnet from Otjosondou, S.W.A.: *Min. Mag.*, **29**, 946-951 (1952).
3. TAYLOR, W. H., DARBYSHIRE, J. A. AND STRUNZ, H., An x-ray investigation of the feldspars: *Zeit. Krist.*, Band **87**, 464-498 (1934).
4. WINCHELL, A. N., Elements of Optical Mineralogy, Part 2, 3rd. Edition. John Wiley and Sons, New York (1945).
5. BAUER, L. H. AND PALACHE, C., Hyalophane from Franklin Furnace, New Jersey: *Am. Mineral.*, **11**, 172-174 (1926).
6. YOSIMURA, T., On barium feldspar from Kaso mine, Tochigi: *Jour. Fac. Sci. Univ. Hokkaido*, Ser. 4, vol. **4**, Nos. 3 and 4, 364-385 (1939).
7. STRANDMARK, J. E., Bidrag till Kännedomen om celsian och andra baryt- fältspater: *Geol. Förel., Förel. Stockholm*, **25**, 289-318 (1903).
8. CLAISSE, F., A roentgenographic method for determining plagioclases: *Am. Mineral.*, **35**, nos. 5 and 6, 412-420 (1950).

NOTES AND NEWS

GENTHELVITE CRYSTAL FROM EL PASO COUNTY, COLORADO

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AND

JOHN W. ADAMS, *U. S. Geological Survey, Denver, Colorado.*

The St. Peters Dome—Stove Mountain area near Colorado Springs, El Paso County, Colo., has been the source of many unusual minerals found in pegmatites in the Pikes Peak granite. One of the rarer minerals of these pegmatites is genthelvite, the zinc member of the helvite group. Until recently this species was represented only by a single small specimen discovered in the 1890's and now in the Genth Collection at Pennsylvania State College, State College, Pa.

In March 1949 J. W. Adams, accompanied by Edwin Over of Colorado Springs, made a brief visit to the area, and in excavating a small miarolitic pegmatite he discovered a large crystal of genthelvite, apparently the largest known crystal of any member of the helvite group. This crystal is 5.5 cm long, 4 cm thick, and weighs 72 grams. It is a somewhat distorted combination of the positive and negative tetrahedrons with narrow rounded faces of the rhombic dodecahedron. Because the combined positive and negative tetrahedrons form a geometrical octahedron, this crystal simulates a distorted octahedron. The tetrahedral faces of this crystal are etched; those of one tetrahedron are more etched than those of the other.

The genthelvite-bearing pegmatite is on a ridge west of the Gold Camp Road (Corley Mountain Highway) in the NW $\frac{1}{4}$ sec. 4, T. 15 S., R. 67 W., El Paso County, Colo. The pegmatite, except for the presence of genthelvite, is similar to many other pegmatites in the area. Although not completely exposed, it appears to have been originally a small cavernous body about 6 feet long and probably not more than 1 foot in diameter. The bulk of the pegmatite material forms a shell about 2 inches thick on the walls that enclose a central miarolitic cavity. This shell consists of a graphic intergrowth of microcline-perthite and quartz, and the cavity walls are lined with projecting crystals of pale buff microcline-perthite and smoky quartz. A few crystals of brown zircon are embedded in the perthite. The cavity is partly collapsed and filled with soil, limonitic mud, and smoky quartz crystals that have become detached from the walls. The genthelvite crystal was found loose in this debris. It is shown in Fig. 1.

Genthelvite is the zinc-rich member of the helvite group, which con-

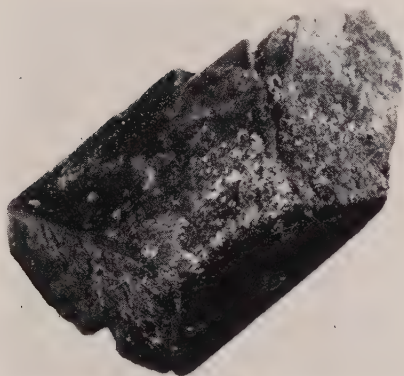


FIG. 1. Photograph of genthelvite crystal from El Paso County, Colo., looking down on a binary axis of symmetry. (Approximately natural size.)

sists of three isomorphous species whose chemical composition is expressed by the general formula $R_4Be_3Si_3O_{12}S$, in which R represents Mn in helvite, Fe in danalite, and Zn in genthelvite.

Frederick A. Genth¹ analyzed and described this zinc-rich member of the helvite group, and called it "a variety of danalite." Although the helvite group has been recognized as a three-component system, later writers overlooked Genth's analysis (published in 1892) of this "danalite" with 46% ZnO. It was not until 1944,² when a detailed study of the helvite group was made, including a re-examination of the original material from the Genth Collection, that the zinc end-member of the helvite group was established and given the name genthelvite.

The crystal is dark reddish brown but thin fragments in transmitted light are pale pink to nearly colorless. Cleavage traces are parallel to the tetrahedron. Fracture uneven. Brittle. Hardness greater than 6. Luster vitreous on fresh surfaces. Sp. gr. = 3.59.³

The mineral is isotropic. Transparent. The index of refraction $n = 1.744$.

Chemical tests showed that the mineral is decomposed by hydrochloric acid, giving off hydrogen sulfide and yielding gelatinous silica. Confirmatory tests for zinc and beryllium were obtained in the U. S. Geological Survey laboratories. Fragments from this crystal assumed a brilliant canary-yellow color due to the arsenic sulfide formed when tested

¹ Genth, F. A., Contributions to mineralogy, No. 54, with crystallographic notes by S. L. Penfield: (6) Danalite: *Am. Jour. Sci.*, **44**, 385 (1892).

² Glass, J. J., Jahns, R. H., and Stevens, R. E., Helvite and danalite from New Mexico, and the helvite group: *Am. Mineral.*, **29**, 163-191 (1944).

³ Specific gravity was determined on the Berman microbalance by Theodore Woodward of the U. S. Geological Survey. Nine determinations were made on six chips and the average computed.

by the Gruner⁴ staining method, a simple test for the identification of any mineral of the helvite group.

X-ray examination by F. A. Hildebrand of the U. S. Geological Survey of genthelvite from El Paso County, Colo., confirms the identity of genthelvite.

This crystal is deposited in the U. S. National Museum.

A XONOTLITE OCCURRENCE IN PUERTO RICO¹

CLIFFORD A. KAYE²

Xonotlite, a relatively rare hydrous calcium silicate, $\text{Ca}_3\text{Si}_3\text{O}_8(\text{OH})_2$ (Berman, 1937, p. 391), has been found in Puerto Rico in an unusual contact association with serpentine and a metavolcanic rock. The mineral was recognized by Robert Berman and Evelyn Cisney, U. S. Geological Survey, using optical and x-ray methods, respectively, from samples collected by the writer.

The xonotlite was discovered in the walls of a tunnel connecting the Rio Yauco and the Rio Loco, not far from the town of Yauco, Puerto Rico. This tunnel is part of the Southwestern Puerto Rico Project of the Puerto Rico Water Resources Authority. The xonotlite occurs approximately 2,000 feet from the outlet portal of the tunnel on the Rio Loco, at the contact of a large serpentine massif and a metavolcanic rock. The mineral was also identified at the surface outcrop of the contact about 150 feet above the tunnel.

The serpentine massif crops out over an area of about 35 square miles and is the largest serpentine body in Puerto Rico. The serpentine exposed in the tunnel is intensely sheared throughout. Its contact with the metavolcanic rock is sharp but uneven in the tunnel; and from its expression on the surface, the contact is seen to be essentially vertical.

The metavolcanic rock has been altered beyond precise recognition at the contact, but it possibly is related to a trachyte that occurs in a relatively fresh state several hundred yards away from the contact. The metavolcanic rock is finely porphyritic with an aphanitic groundmass. At the contact the phenocrysts are augite and feldspar, the latter mineral being completely altered to a variety of chlorite. The matrix, which in hand specimens is white, is seen under the microscope to be a very fine-grained aggregate of slightly brownish material of very low birefringence. It is probably a clay. Farther away from the contact the clayey ground-

⁴ Gruner, John W., Simple test for the detection of the beryllium mineral helvite: *Econ. Geol.*, **39**, 444-447 (1944).

¹ Publication authorized by Director, U. S. Geological Survey.

² Geologist, U. S. Geological Survey, Spokane, Washington.

mass is rich in fine pyroxene needles, and the color of the rock matrix is dark olive gray.

The xonotlite lines the serpentine-metavolcanic contact as disconnected masses and pods, as much as 3 inches thick. The mineral is found only at the contact and does not penetrate either of the wall-rocks. It possesses the characteristic physical and optical properties that have generally been ascribed to xonotlite. Optically, it is colorless, acicular, and biaxially positive, having indices of $\alpha=\beta=1.581$ and $\gamma=1.591$. Its acicular habit makes a positive measurement of the $2V$ doubtful. The mineral exhibits parallel extinction. Physically it has a hardness of 6 and is unusually tough.

The xonotlite exhibits the following three, rather distinctive habits:

(1) *Massive habit*. Found only in a few places and only where the xonotlite is 2 inches or more thick. It apparently consists of randomly oriented small crystals. Individual crystals are not apparent to the naked eye. The mineral aggregate is light gray to medium gray and has a slightly greasy luster.

(2) *Parallel-fibrous, translucent xonotlite*. This is the most common form of xonotlite found. The long, fibrous crystals are too thin to be distinguished individually with the naked eye. The color varies from medium gray to very light gray. Only one small spot was seen with the flesh-pink coloration that reportedly characterizes freshly broken xonotlite (Foshag and Larsen, 1922; Schwartz, 1924, 1925; and Shannon, 1925). At right angles to the fiber direction, the mineral has a sharp hackly fracture and a dull glassy luster. Parallel to the fiber direction the luster is slightly pearly. Specimens in the writer's possession more than two years have lost some of their translucency and have developed white streaks.

Of interest is the fact that the fiber direction lies in the plane of the contact and is generally parallel to the slickensides, which everywhere score the contact surface.

(3) *Chalky white, acicular habit*. The luster varies from chalky to pearly. This form of the mineral is somewhat less tough than the other forms and breaks rather easily, producing a splintery fracture in which the needle-like crystals are evident. This variety of xonotlite commonly occurs as thin layers between the fibrous translucent variety and the wallrock. It is probably an alteration product of the other varieties.

The only other vein mineral noticed in the vicinity of the contact was prehnite, which occurs as small veins in the metavolcanic rock.

Several hypotheses may explain the origin of the xonotlite deposit. One is that the xonotlite was formed along the contact during the shearing movement that slickensided the wallrock. The orientation of most of

the xonotlite crystals parallel to the slickensides strongly suggests a genetic relationship between the mineral crystallization and the displacement along the contact. Possibly the heat generated by this movement was sufficient to alter a pre-existing calcite vein into the hydrous calcium silicate, xonotlite, in the presence of siliceous emanations from the serpentine. The calcite may have been deposited at the contact in a pre-movement stage. A possible alternative to this hypothesis is that the xonotlite formed prior to the movement along the contact but that this movement caused recrystallization of the original xonotlite into the parallel-fibrous variety. The massive xonotlite described above would thus be relict from the pre-movement deposit. In any event, the origin of the xonotlite apparently is related to emanations from the serpentine. The fact that the xonotlite is confined to the contact plane and does not penetrate the wallrock indicates, however, that conditions at the contact were critical to its formation.

REFERENCES

- BERMAN, HARRY (1937), Constitution and classification of the natural silicates: *Am. Mineral.*, **22**, 342-408.
- FOSHAG, W. F., AND LARSEN, E. S. (1922), Eakleite from Isle Royale, Michigan: *Am. Mineral.*, **7**, 23-24.
- SCHWARTZ, G. M. (1924), An occurrence of xonotlite in Minnesota: *Am. Mineral.*, **9**, 32-33.
- (1925), Xonotlite and pectolite in a diabase pegmatite from Minnesota: *Am. Mineral.*, **10**, 83-88.
- SHANNON, E. V. (1925), An occurrence of xonotlite at Leesburg, Virginia: *Am. Mineral.*, **10**, 12-13.

CUMMINGTONITE FROM THE MIKONUI RIVER,
WESTLAND, NEW ZEALAND

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Cummingtonite has not been recorded from New Zealand, although a considerable part of the South Island is made up of metamorphic rocks of various kinds. However, large areas of these rocks are situated in the geologically little explored region of the Southern Alps. Some years ago I collected a number of boulders of unusual appearance from the rivers draining the Southern Alps in Westland. Recent examination has shown the presence of abundant cummingtonite in some of these.

The cummingtonite-bearing boulders were collected from the Mikonui River where the main road crosses it just south of the town of Ross. The boulders were well rounded and ranged up to two feet in diameter, a not uncommon size in these swift mountain torrents. These boulders have a typically rusty surface, evidently due to the partial decomposition of the iron-bearing minerals. On breaking them with a ham-

mer, they split comparatively easily along cummingtonite-rich surfaces. Other minerals visible to the unaided eye are quartz, dark-red garnet, and small amounts of pyrrhotite and a black bladed mineral, later identified as ilmenite. The rock can best be described as a quartz-rich cummingtonite-garnet schist. In some specimens the schistose structure is not pronounced, and the rock could be called a cummingtonite-garnet quartzite.

The cummingtonite occurs as fibrous radiating aggregates of crystals, the individual crystals being up to 20 mm. long. Its color is pale clove brown. The hardness is about 5. The density (measured by suspension in Clerici solution) is 3.27.

In thin sections under the microscope the cummingtonite appears as long fibrous crystals containing numerous inclusions of quartz crystals elongated in the c direction of the cummingtonite. The color is pale yellowish-gray, and the mineral shows feeble pleochroism, the intensity of color being greatest in the Z direction. Some crystals show polysynthetic twinning. The extinction is oblique, the extinction angle ($Z \wedge c$) being 16° . The interference figure indicated a high axial angle, and this was confirmed by universal stage measurements, which showed that the sign is positive and that $2V = 86^\circ$. Refractive indices (measured in sodium light by the immersion method) are $\alpha = 1.651$, $\gamma = 1.678$; $\gamma - \alpha = 0.027$. From the axial angle and the measured values of α and γ , the calculated value of β is 1.664. From the data given by Bowen and Schairer (1935) this indicates a cummingtonite with almost 50% of the $\text{Mg}_7(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$ component, a figure which was confirmed by chemical analysis.

A pure sample of cummingtonite for chemical analysis was readily separated from the crushed rock by centrifuging the 140–400 mesh fraction in methylene iodide-acetone mixtures. The separated material was examined under the microscope and found to be 99%+cummingtonite, the only impurity being tiny quartz inclusions. The analysis (Table 1) was made by Mr. M. Coller, analyst in the Department of Geology of Indiana University, to whom I would express my appreciation for his careful work. Fluorine was tested for and not found. The first determination of $\text{H}_2\text{O}+$ by the Penfield method, with ignition at red heat for five minutes, gave 0.66%, clearly a low figure in view of the accepted amphibole formula. Redetermination with ignition for 30 minutes raised this figure to 1.04%, still below the theoretical quantity ($\pm 2\%$). This experience confirms the belief held by some chemists and mineralogists that Penfield method fails to drive off all the combined water in minerals which hold this water very tenaciously, such as the amphiboles. Rabbitt (1948) mentions a similar experience in his study of the anthophyllite series.

In Table 1 the analysis (after subtracting an estimated 1% SiO_2 as quartz impurity) is recalculated into atoms per unit cell, according to the procedure recommended by Hey (1939), using the measured density of 3.27 and a figure of $909 \text{ \AA}^3$ for the volume of the unit cell. The results show good agreement with the accepted formula of cummingtonite, $(\text{Fe,Mg})_{14}(\text{Si}_4\text{O}_{11})_4(\text{OH})_4$, except for the deficiency in OH, this being apparent rather than real, due to the incomplete removal of water by the Penfield method. The analysis shows the typical features of other analyzed cummingtonites, especially a low content of Al, which seems to be characteristic of this amphibole. Compared with other analyzed cummingtonites, the Mikonui material is closest in composition to one from Isopää, Finland, described by Eskola (1936).

TABLE 1. ANALYSIS OF CUMMINGTONITE

Analysis		atoms per unit cell			
SiO_2	52.9	Si	15.64	Si+Al	16.00
TiO_2	0.06	Al	0.84		
Fe_2O_3	0.0	Fe	7.08		
Al_2O_3	2.37	Mg	6.18	Al+Fe+Mg	
FeO	28.0	Ca	0.18	+Ca+Mn	14.17
MgO	13.71	Mn	0.25		
CaO	0.55	O	44.14		44.14
MnO	0.97	OH	2.10		2.10
$\text{H}_2\text{O} > 105^\circ$	1.04				
Na_2O^*	<0.1				
F	<i>not found</i>				
Total	99.60				

* By spectrographic analysis.

Some confusion exists in the naming of amphiboles of this composition, since the names cummingtonite and grünerite have been used by different mineralogists for what is actually a single phase. Sundius (1931) has suggested that the name cummingtonite be limited to material containing 50-70 mole per cent of the magnesium component, and that the varieties richer in iron be called grünerite. This proposal would have the curious result of requiring the original cummingtonite from Cummington, Massachusetts, to be called grünerite. Since one name is adequate for this amphibole species (or sub-species) and cummingtonite has clear priority (cummingtonite: Dewey, 1824; grünerite: Kenngott, 1853), the name cummingtonite should be accepted and grünerite relegated to the synonymy. If it is necessary to distinguish the magnesium-rich varieties this can be accomplished by the use of an adjectival prefix, i.e. magnesian cummingtonite.

Since the cummingtonite was collected in a stream boulder and not observed in place, little can be said about its geological occurrence. Morgan's description of the Mikonui Subdivision (1908) shows that the Mikonui River drains larger areas of schists of the Arahura Series. None of the rocks he describes resembles the material discussed in this paper and this probably means that it is of comparatively local occurrence. The essential minerals of the rock are cummingtonite, quartz, and garnet, the cummingtonite and garnet in sub-equal amounts and the quartz in excess of either. Feldspar is totally absent. The garnet has $n=1.81$, $D=4.09$, and lattice dimensions $a_0=11.59 \text{ \AA}$; a spectrographic analysis showed that the major elements are Fe, Si, and Al, with minor Ca and small amounts of Mg and Mn. These properties indicate that the garnet is essentially an almandite, with about 30% of the grossularite component. The mineralogical assemblage quartz-cummingtonite-almandite places this rock either in the amphibolite facies or the epidote—amphibolite facies. The general appearance of the rocks of the Arahura Series suggest that they belong to the lower rather than the higher of these two facies, although rocks belonging to the amphibolites facies may be developed around the granite intrusions which are common in the Mikonui Valley. Prior to metamorphism the quartz-garnet-almandite rock may have been a sandstone with clayey and ferruginous impurities; on the other hand the rock may be of metasomatic origin. This question can only be settled when the rock is found in situ. A small amount of later alteration is indicated by the beginning alteration of almandite to chlorite along cracks.

REFERENCES

- BOWEN, N. L., AND SCHAIRER, J. F. (1935), Grünerite from Rockport, Massachusetts, and a series of synthetic fluor-amphiboles: *Am. Mineral.*, **20**, 543–551.
- DEWEY, C. (1824), A sketch of the geology and mineralogy of the western part of Massachusetts, and a small part of the adjoining states: *Am. J. Sci.*, **8**, 1–60.
- ESKOLA, P. (1936), A paragenesis of gedrite and cummingtonite from Isopää in Kalvola, Finland: *Bull. Comm. Geol. Finlande*, No. **115**, 475–487.
- HEY, M. H. (1939), On the presentation of chemical analyses of minerals: *Mineral. Mag.*, **25**, 402–412.
- KENNGOTT, G. A. (1853), Das Mohs'sche Mineralsystem, p. 69.
- MORGAN, P. G. (1908), The geology of the Mikonui Subdivision, North Westland: *New Zealand Geol. Surv. Bull.* No. **6**.
- RABBITT, J. C. (1948), A new study of the anthophyllite series: *Am. Mineral.*, **33**, 263–323.
- SUNDIUS, N. (1931), Optical properties of grünerites and cummingtonites: *Am. J. Sci.*, **221**, 330–344.

TRIDYMITITE AND CHRISTENSENITE

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In 1944 Barth and Kvalheim described a mineral from a lava from Deception Island as a solid solution of about 5% NaAlSiO_4 in SiO_2 , with the tridymite structure, and gave it the name christensenite, to distinguish it from "pure" tridymite, which they presumably consider as 100% SiO_2 . The purpose of this note is to point out that the original tridymite from Cerro San Cristobal, Pachuca, Mexico, also contains Al, Na, and other elements in solid solution, and that this is probably the case with all natural tridymites. Under these circumstances the name christensenite seems superfluous.

The two analyses of the original tridymite from Pachuca published by vom Rath (1868) show 96.1% and 95.5% SiO_2 , the remainder being reported as ferric oxide, alumina, magnesia, and loss on ignition; the presence of sodium and potassium was also established. Vom Rath evidently considered tridymite to be pure SiO_2 , and believed that most of the ferric oxide was derived from the steel mortar in which the material was crushed, and that the remainder, together with the magnesium, alumina, and alkalis, represented admixed rock material, although he stated that several days were spent in selecting pure material for analysis. During a visit to Mexico in 1950 I took the opportunity of collecting some specimens of the tridymite-bearing andesite from the type locality at Pachuca. Pure tridymite was separated from this material by density and magnetic separation, and was analyzed spectrographically by Mr. R. K. Leininger, of the Indiana Geological Survey, to whom I would express my grateful thanks. This analysis gave the following percentages: Al_2O_3 2.4, Fe_2O_3 0.36, MgO 0.3, CaO 0.4, TiO_2 0.26, Na_2O 0.80, K_2O 0.37, MnO 0.003, SiO_2 by difference 95.1. When this analysis is recalculated into atomic percentages it is found that $2\text{Ca} + \text{Na} + \text{K}$ equals Al within the probable error of the analysis; i.e., if Al^{3+} replaces Si^{4+} in the tridymite lattice, electrical neutrality is preserved by the introduction of an equivalent amount of calcium, sodium, and potassium cations in vacant positions in the tridymite lattice.

A similar result was obtained with tridymite from a trachyte dike near Lyttleton, New Zealand. Tridymite separated from this rock and purified by density and magnetic separations gave the following analysis: Al_2O_3 2.7, Fe_2O_3 0.25, MgO 0.4, CaO 0.2, TiO_2 0.28, Na_2O 0.67, K_2O 0.75, MnO 0.0005, SiO_2 by difference 95.1. This analysis shows a close similarity to that of the tridymite from Pachuca. Again there is a balance be-

tween the amount of aluminum and that of the alkali and alkaline earth elements, which corroborates the hypothesis that the aluminum is replacing silicon and the alkali and alkaline earth cations make up the resulting charge deficiency by entering vacant lattice positions. The few published analysis of tridymite from other localities also indicate that natural tridymite is never pure SiO_2 , in contrast to quartz.

Barth and Kvalheim remark that the optical properties of the Deception Island mineral support the view that it is a solid solution of NaAlSiO_4 in SiO_2 ; its refractive indices are considerably higher than those of synthetic tridymite made from pure SiO_2 , β for the Deception Island material being 1.480, in contrast to $\beta=1.470$ for the synthetic material. The Pachuca and Lyttleton tridymites show the same phenomenon, β being 1.478 in each of these. Barth and Kvalheim pointed out that tridymite from Japanese lavas also has higher refractive indices than those of synthetic tridymite, and Durrell (1940) recorded the following indices for tridymite from andesite near Portola, Plumas County, California: $\alpha=1.478$, $\beta=1.479$, $\gamma=1.481$.

Thus all the evidence indicates that the original tridymite, and all natural tridymites, are not pure SiO_2 , but contain aluminum and alkali and alkaline earth elements in solid solution. In view of the ability of the tridymite lattice to accommodate foreign ions, it is quite unlikely that pure SiO_2 will crystallize in the tridymite lattice in any natural environment, where foreign ions are universally present. Buerger (1935) has pointed out that tridymites in lavas have probably been deposited outside the stability field of pure SiO_2 tridymite, the stabilizing factor being the presence of large cations buttressing the open tridymite lattice. There is no essential difference between the original tridymite from Pachuca and that from Deception Island and hence no occasion for the introduction of a new mineral name on this account. The name christensenite is therefore superfluous.

REFERENCES

- BARTH, T. F. W., AND KVALHEIM, A. (1944): *Scientific results of the Norwegian Antarctic expeditions 1927-1928*, no. 22, 9 pp.
BUERGER, M. J. (1935): *Zeit. Krist.*, **90**, 186-192.
DURRELL, C. (1940): *Am. Mineral.*, **25**, 501-502.
VOM RATH, G. (1868): *Ann. Phys. Chem.*, **136**, 437-454.

ROENTGENITE, $3\text{CeFCO}_3 \cdot 2\text{CaCO}_3$, A NEW MINERAL
FROM GREENLAND*

GABRIELLE DONNAY, *U. S. Geological Survey, Washington 25, D. C.*

In the course of an *x*-ray study of bastnaesite (CeFCO_3), parisite ($2\text{CeFCO}_3 \cdot \text{CaCO}_3$), and synchisite ($\text{CeFCO}_3 \cdot \text{CaCO}_3$), a new species, $3\text{CeFCO}_3 \cdot 2\text{CaCO}_3$, was found and named *roentgenite*. A description of the relations of this mineral to the others will appear in this journal in the near future. The purpose of this note¹ is to put on record the properties of roentgenite itself.

CRYSTALLOGRAPHY: Hexagonal—*R*. Trigonal pyramidal, 3.

Axial ratio: $c/a = 9.74 \pm 0.03$.

FORMS:

	ϕ	ρ
<i>c</i> 0001	—	0°00'
<i>q</i> 10 $\bar{1}$ 1	30°00'	84°55' (calc., poor reflection)
<i>p</i> 01 $\bar{1}$ 2	—30°00'	79°55' $\pm 2'$ (meas.: 79°54', 54', 56', 57')

{0001} is always small so that it may be written {0003}. All observed forms then obey the rhombohedral criterion: $-h+k+l=3n$.

CLEAVAGE: No cleavage is observed.

STRUCTURE: Laue class $\bar{3}$; diffraction aspect R^{**} . The center of symmetry is ruled out by twinning (see below) and because the structure is closely related to that of bastnaesite, which is strongly piezoelectric (Ofstedal, 1931, p. 465). The space group is therefore $R3$ (C_3^4). Cell dimensions: $a_0 = 7.131 \pm 0.02$ Å, $c_0 = 69.41 \pm 0.2$ Å, $c_0/a_0 = 9.73_3$. Cell contents: 9 ($3\text{CeFCO}_3 \cdot 2\text{CaCO}_3$). A pronounced pseudo-cell has pseudo-space group $C\bar{6}m2$; $a' = a_0/\sqrt{3} = 4.11_7$ Å, $c' = c_0/3 = 23.1_{35}$ Å, $Z = 1$. Another, smaller, pseudo-cell has diffraction aspect C^{***} ; $a' = 4.11_7$ Å, $c'' = c'/5 = 4.62_7$ Å. The structure consists of horizontal layers, in which cerium and fluorine ions alternate at the corners of hexagons. Vertical and nearly vertical carbonate groups separate these layers from each other and from calcium layers. Calcium ions lie above cerium ions (Fig 1).

HABIT: Similar to that of parisite and synchisite. Most crystals are singly terminated, with *q* and *p* dominant, truncated by a small monohedron *c*. The two pyramids are striated horizontally (Fig. 2).

TWINNING: Twinning by reticular merohedry, uncommon, defined by reflection in twin plane and composition plane (0001). Twins are doubly terminated, showing twin symmetry $\bar{6}$ or $\bar{6}m2$, which rules out $\bar{3}$ as a possible point group.

* Publication authorized by the Director, U. S. Geological Survey.

¹ This work was done on behalf of the Division of Research of the U. S. Atomic Energy Commission.

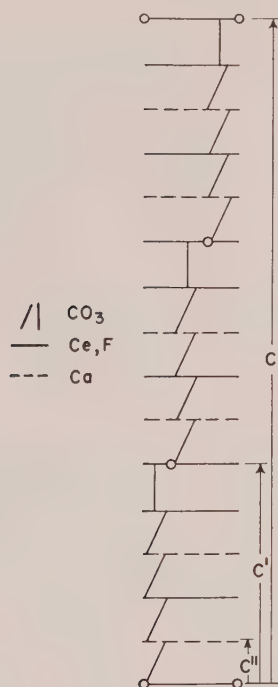


FIG. 1. Schematic presentation of the crystal structure of roentgenite. Rhombohedral lattice points shown along diagonal of rectangle.

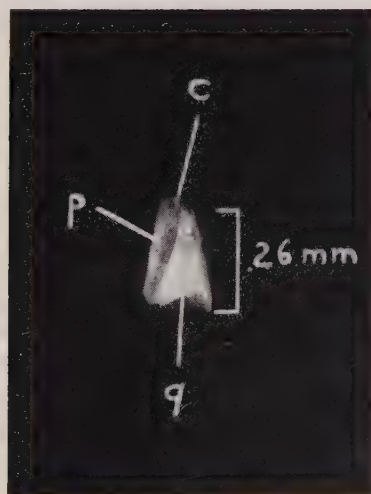


FIG. 2. Roentgenite crystal showing forms $q\{10\bar{1}1\}$, $p\{01\bar{1}2\}$, and $c\{0003\}$.

PHYSICAL PROPERTIES: The fracture is subconchoidal. Crystals are transparent to translucent and wax-yellow to brown. The crystals were too small for the specific gravity to be determined experimentally; the calculated value is 4.19.

OPTICAL PROPERTIES: Colorless to light yellow in transmitted light. Uniaxial positive; $\omega = 1.662 \pm 0.002$, $\epsilon = 1.756 \pm 0.005$ (in sodium light). The indices were measured by H. W. Jaffe of the U. S. Geological Survey.

CHEMICAL COMPOSITION: Because of the almost universal intergrowth of this mineral with bastnaesite, parisite, or synchisite, not enough pure material was available for a chemical or even a spectrographic analysis. The composition was obtained as follows, from a plot of cell dimension c'' (in Å) vs. composition (CaCO_3 in mol %). The c'' values for bastnaesite (4.894) and parisite (4.673) are plotted, and a straight line is drawn through them. The observed c'' of roentgenite corresponds exactly to 40.0 mol % CaCO_3 so that the formula is $3\text{CeFCO}_3 \cdot 2\text{CaCO}_3$. The fact that the observed c'' of synchisite (4.566) corresponds exactly to 50.0 mol % CaCO_3 indicates that the linear relationship is indeed obeyed. The composition is further confirmed by the crystal structure and the refractive indices, $\omega = 1.654$, $\epsilon = 1.755$, calculated from it. These indices are obtained from the relations.

$$\frac{\epsilon^2 - 1}{\epsilon^2 + 2} \cdot \frac{MW}{G} = \sum_i (R_\epsilon)_i N_i; \quad \frac{\omega^2 - 1}{\omega^2 + 2} \cdot \frac{MW}{G} = \sum_i (R_\omega)_i N_i$$

where MW is the molecular weight, G the specific gravity, R_ϵ (or R_ω) the ionic refractivity, and N_i the number of atoms of the i^{th} element in the molecule.

Cerium is presumably replaced by other rare earths, as this is known to be the case in the associated minerals.

TESTS: Crystals dissolve in strong acids, for instance 6N HNO_3 . In solubility roentgenite is intermediate between synchisite and parisite.

OCCURRENCE: Roentgenite occurs intimately associated with synchisite, parisite, and bastnaesite at Narsarsuk, Greenland. Syntaxic intergrowths with each of the other species are common; they simulate single crystals. The boundary surface between the two species is planar, or irregular, or both.

The work reported was done on material kindly supplied by the U. S. National Museum (Specimen Nos.: R2609, R2613, and R2615) and the Harvard University Museum (No. 84233).

NAME: The mineral is named after Wilhelm Konrad Roentgen (1845–1923), discoverer of x-rays, because x-ray methods alone proved its existence and established its formula.

REFERENCE

OFTEDAL, I. (1931), Zur Kristallstruktur von Bastnäsit: *Zeits. Krist.*, **78**, 462–469.

It has been announced by Paul T. Allsman, Regional Director Region V, that a new laboratory pilot plant for the recovery of beryl, a rare and critical mineral with many military and industrial uses, found in South Dakota's rich Black Hills, will begin its first test run in the Pegmatite Research Laboratory of the U. S. Bureau of Mines, Department of the Interior, in Rapid City. Laboratory tests at Rapid City have indicated that ore as low as 0.1 per cent beryl can be successfully concentrated with a recovery of 85 per cent. In recent years, South Dakota has produced about 100 tons of beryl annually—approximately 50 per cent of domestic production.

The Ohio State University conferred the degree of Doctor of Science on William J. McCaughey, Professor Emeritus of Mineralogy, in recognition of his contributions through the teaching of applied mineralogy. The degree was conferred at Columbus on June 12, 1953.

The Eleventh Annual Pittsburgh Diffraction Conference will be held at Mellon Institute, Pittsburgh, Pa., on November 5 and 6, 1953. Technical sessions are being arranged on *Instrumentation and Methods, Metals, Recrystallization and Preferred Orientation, and Structure of Polymers*. Papers on general diffraction subjects will also be accepted.

Contributed papers will be considered in the order in which they are received. Titles should be submitted to the Program Chairman, Mr. E. E. Wicker, United States Steel Corporation, Research and Development Laboratory, 234 Atwood Street, Pittsburgh 13, Pa., before September 1, 1953. Abstracts should be submitted by September 21. For further information, and for a copy of the preliminary program when available, write to Dr. H. R. Letner, Mellon Institute, Pittsburgh 13, Pa.

The American Geological Institute has announced the appointment as its Executive Director Mr. C. B. Hunt, currently Chief of the General Geology Section of the U. S. Geological Survey with headquarters in Denver, Colorado. He assumed his new duties on Sept. 1, 1953. Also the appointment of Dr. H. Richard Gault to serve as Executive Secretary of the Division of Earth Sciences has been announced by the Academy Council. His appointment became effective July 1.

On October 1, 1953, the Mineralogical Society of Philadelphia is devoting a meeting to the memory of Samuel G. Gordon. Dr. W. Parrish will be the scheduled speaker; he will talk on "Gordon's contribution to mineralogy."

Dr. Fred. E. Wright, petrologist of the Geophysical Laboratory from 1906 to his retirement in 1944, president of the Mineralogical Society of America in 1941 and recipient of the Roebling Medal in 1952, died at his summer home in Gananoque, Ontario, on Aug. 25, 1953, at the age of 75 years.

Albert A. Klein, assistant director of research at the Norton Company, suffered a heart attack and died Aug. 25, at the age of 64. Mr. Klein's special interests included microscopic and x-ray techniques as applied to bonded abrasives and refractories.

MINERALOGICAL SOCIETY (LONDON)

A meeting of the Society was held on Thursday, June 11th, 1953, at 5 P.M., in the apartments of the Geological Society of London, Burlington House, Piccadilly, W.1 (by kind permission).

The following papers were read:

(1) A LARGE MINERALIZED CAVITY IN A THOLEIITE DIKE IN NORTHUMBERLAND.

By Mr. B. A. O. Randall.

A remarkable, large and mineralized cavity in a tholeiite dike at Sleekburn colliery, Bedlington, Northumberland, is described and other cavities in dikes in the N.E. coalfield are recorded. The Sleekburn cavity shows mineralized walls with pyrite, marcasite, ankeritic calcite and ankeritic dolomite in horizontal zones. The cavity is thought to owe its origin to gasification of coal caught up in the dike and the minerals to have been transferred to it from the surrounding strata by ground waters at low temperature.

(2) AN INVESTIGATION OF HIGH-TEMPERATURE OPTICS IN SOME NATURALLY OCCURRING PLAGIOCLASES.

By Dr. Olive Bradley.

Plagioclase crystals from several natural sources (including pitchstones) have been studied by optical methods. The results suggest that a transition series between the high and low-temperature forms is possible, and confirm that plagioclase composition determinations by universal stage methods only are unreliable.

(3) A SIMPLE MONOCHROMATOR.

By Mr. H. C. G. Vincent (communicated by the General Secretary).

An easily constructed and inexpensive monochromator is described. White light, after passing through an adjustable slit, is rendered parallel and dispersed by two hollow prisms in series containing α -monochloro-naphthalene. From the wide spectrum so produced any desired wave band may be selected on a calibrated arc, with settings independent of temperature and other variables.

(4) A RAPID METHOD FOR THE PRODUCTION OF THIN ROCK SECTIONS.

By Mr. E. O. Rowland (communicated by Dr. A. K. Wells).

A technique is described whereby thin sections of rocks can be prepared much more quickly than by the methods currently employed. It involves the use of an ordinary type of surface grinding machine, fitted with a diamond-impregnated wheel. The process is mechanical almost throughout, and the finished sections are in no way inferior to those produced by hand.

(5) A NOTE ON THE OCCURRENCE OF BERYL AND LÖLLINGITE AT THE NEW CONSOLS MINE, STOKE CLIMSLAND, CORNWALL.

By Mr. P. G. Embrey.

(6) NOTES ON THE OCCURRENCE OF COSALITE AND OTHER LEAD SULPHO-SALTS AT GRAINSGILL, CALDBECK, CUMBERLAND.

By Mr. A. W. G. Kingsbury and Mr. J. Hartley.

Old references to the occurrence of antimonite at Carrock Fell are probably based on faulty identification. Recent examination has proved the occurrence in veins in the greisen

of cosalite ($\text{Pb}_2 \text{Bi}_2 \text{S}_8$), which has not been previously recorded as a British species, boulangerite and jamesonite.

The following papers were taken as read:—

(1) HIGH-TEMPERATURE PHASE CHANGES IN KAOLINITES.

By Dr. Wm. D. Johns.

Thermal transformations of kaolinitic minerals were studied in detail by *x*-ray diffraction and differential thermal analysis. It was shown that the crystallinity of the mullite formed at 1000° C. varies consistently with progressive disorder of the kaolinitic parent material. The dependence of the mullitization process on the disorder of the kaolinite confirms the presence of a poorly organized kaolinite anhydride following dehydroxylation. High-temperature thermal effects are interpreted as being associated with the evolution of energy at the time when slight changes in the octahedrally co-ordinated level of metakaolinite result in mullite-type co-ordination chains. In the case of well-ordered kaolinite, ignition results in the proper distribution of both anions and cations for the crystallization of mullite. In the case of completely disordered kaolinite, only the oxygen packing approaches that of mullite following ignition to 1000° C. In the case of halloysite neither cations nor anions are properly distributed to give mullite.

(2) A SAPONITE FROM KRUGERSDORP DISTRICT, TRANSVAAL.

By Mr. E. R. Schmidt and Mr. H. Heystek (communicated by the General Secretary).

A white, soapy clay mineral occurring in a vein in massive serpentines and amphibolites was investigated by optical, chemical, *x*-ray and differential thermal methods and identified as a saponite. It is a Mg-end member of the montmorillonite group with formula $(\text{Fe}_{0.01}\text{Mg}_{2.99})(\text{Al}_{0.37}\text{Si}_{3.63})\text{O}_{10}(\text{OH})_2 0.18\text{Mg}$ in which 0.18Mg represents exchangeable cations consisting almost wholly of Mg.

(3) ON THE OCCURRENCE OF NACRITE AT SHAP, WESTMORLAND.

By Mr. R. J. Firman.

Nacrite of hydrothermal origin has been identified by *x*-rays in crevices in the andesitic rocks around the Shap granite.

(Titles and abstracts kindly submitted by G. F. Claringbull, General Secretary.)

BOOK REVIEWS

ZUR STRUKTUR UND MATERIE DER FESTKÖRPER. Diskussionstagung der Sektion für Kristallkunde der Deutschen Mineralogischen Gesellschaft am 1./2. Mai 1951 in Frankfurt/M. 1952. Springer-Verlag, Berlin, Göttingen, and Heidelberg. 14×21 cm., v+304 pp., 95 figs. Paper bound, Price DM 28.60 (\$7.00).

In the spring of 1951 the newly founded Section on Crystal Science of the German Mineralogical Society held its first meeting. Outstanding German crystallographers, physicists and chemists, active in far-flung fields, were invited to acquaint mineralogists with the results of their work. The usefulness of such contacts is well demonstrated by the book under review, in which eight lectures are presented together with carefully edited discussions.

The introduction is a welcoming address to the visitors, in which section leader O'Daniel explains the purpose of the meeting. In the first paper (24 pp.) Niggli deals with the symbolism of groups of symmetry operations useful in spectroscopy as well as crystallography. He summarizes a lifetime of work in the field. C. Hermann takes the reader to the realm of n -dimensional translation groups. His crisp mathematical treatment (6 pp.) is not easy to follow for the uninitiated, who will be grateful for the three pages of helpful discussion that follow it. Sublimation of crystals is discussed by Knacke, Stranski, and Wolff (22 pp.). In claudetite theory and observation agree; in arsenolite a strong deformation must be postulated in the interior of the crystal. Kossel (40 pp.) convincingly advocates the use of monocrystalline spheres in the study of surface phenomena, such as etching and crystal growth. A review of his theory on crystal growth is included. Jagodzinski summarizes and expands his work on order-disorder in crystals (31 pp.), a topic which should become increasingly important to mineralogy. There follows a long paper (96 pp.) by Hosemann on the statistical nature of the structure of macromolecules and colloids. The concept of "paracrystals," previously introduced by Kratky and referring to crystals whose lattice vectors vary slightly from unit cell to unit cell, is found useful. Smekal surveys our knowledge of the structure of solids in the glassy state, and the conditions under which they form and persist in metastable states. Many points of interest to the mineralogist are covered by him (49 pp.). In the last contribution (32 pp.) Witte tells of new experiments on the influence of Brillouin Zones on physico-chemical properties of alloys.

The papers are not grouped around one subject and the bearing of some of the topics on mineralogical problems is as yet remote. This statement, however, is not intended as an adverse criticism—understanding of basic crystallographic problems will make for better mineralogy.

GABRIELLE DONNAY

ROCKS FOR CHEMISTS, AN INTRODUCTION TO PETROLOGY FOR CHEMISTS AND STUDENTS OF CHEMISTRY, by S. JAMES SHAND, New York, Pitman Publishing Corporation, 1952, xii+146 pages; 32 plates. Price, \$4.50.

In this little volume Shand recognizes and tries to do something about one of the great problems of modern science—cooperation among disciplines where specialization has taken a subject as far as it can go without help. It has been realized for decades that petrology has gone about as far as field studies, descriptions, and classifications can take it without more fundamental data on which to base interpretations. Fortunately, some of the foremost chemists of the day have turned their attention to these problems, with gratifying results. If this book succeeds in interesting other chemists in Nature's great laboratory with its

innumerable chemical problems, to the point of helping solve some of them, it will have been eminently worthwhile.

The above point of view is outlined in a 2-page Preface, which is followed by a brief Historical Introduction. There are short chapters on Rocks in the Field, Rock-forming Minerals, The Nature of Active Lava, The Nature of Underground Lava, and The Classification of Eruptive Rocks. The eruptive (igneous) rocks are then discussed in seven chapters covering 61 pages. One chapter of 12 pages is devoted to Rock Weathering and Sedimentary Rocks; metamorphic rocks and processes are allotted 2 chapters comprising 20 pages.

The book is well written and nicely printed; it should appeal to a much wider audience than just the chemical fraternity, for whom it was written. The splendid plates (photographs of field occurrences, hand specimens, and thin sections of rocks) lose some of their effectiveness by being grouped together at the back of the book so that reference to them from the text is inconvenient. The index of $2\frac{1}{2}$ pages is unnecessarily short; it contains no names of authors or localities and so is little more than a list of the minerals and rocks discussed, with a few important subject headings thrown in for good measure.

As one would expect, most of the statements in the book are petrologically and chemically sound. Here and there, however, inaccuracies have crept in. Some of these are merely failures to consider the more recent literature on a subject. For example, the 1921 statement by Shepherd on the plutonic origin of volcanic gases, quoted on page 23, was modified later (1938) when Shepherd came to realize the variable, but considerable contamination of such gases on their way to the surface. The measurements of temperatures of lava cited on page 25 are badly out of date now, as are the methods of making them. Recent measurements with optical pyrometers have given much more reliable results. The temperature of 1350° mentioned in paragraph 2 on page 27 for fire fountains must represent local flame temperatures; no lava that hot has ever been measured.

There are a few statements in the book that are definitely in error. For example, on page 18 reference is made to the escape of hot, highly compressed gas from lava. The gas is not present as a separate phase as the lava ascends, but is actually *dissolved* in the silicate melt. On page 59 it is stated that "even quite siliceous obsidian" occurs in the Hawaiian Islands; no rocks more siliceous than trachytes have been described from the Islands. On page 69 corundum is listed as a constituent of granite pegmatites, but it is incompatible with quartz, as stated on page 39, which occurs in large quantities in such pegmatites.

Other statements, while not actually in error, leave erroneous impressions. For example, on page 18, paragraph 2, and again on page 21, paragraph 2, the impression is created that all of the gas escaping from a lava is combustible, but numerous analyses show the gas to consist almost entirely of H_2O , CO_2 , N_2 , SO_2 , A, and other oxidized or inert gases; commonly only a fraction of one per cent could burn. At the end of the first paragraph on page 20, the volcanic Hawaiian Islands are said to be "arranged along the top of a submarine ridge." It should be emphasized that the "ridge" is merely the bottom part of the immense pile of lava that has poured out along a fissure or structural line of weakness in the floor of the Pacific.

A number of other questions concerning usage and interpretation should be pointed out. It is surprising to find hornblende and melilite grouped together in a classification of rock-forming minerals (p. 14-15). In paragraph 2, page 20, two possibilities are mentioned for the origin of magma reservoirs in the earth's crust; a third alternative—local relief of pressure—is probably more generally accepted today as the mechanism of generating magmas than either of the ones mentioned. In the chapter on classification of eruptive rocks Shand points out the inconsistencies, limitations, and other disadvantages of existing mineralogical and chemical classifications. His criticisms are perhaps a little too severe. On page 67, paragraph 2, the statement is made that the term *granodiorite* is used in America "for any granitic rock holding a rather large proportion of plagioclase." That depends on who uses

the name; some authors stay by Lindgren's original definition, which gives the term a definite and restricted meaning. The last sentence of paragraph 1, page 131, states flatly that metasomatism takes place by migration of ions of Na, K, Ca, and other elements, together with silica, through the medium of intergranular water films; at present there is not even agreement as to the reality of migration of ions through solid rocks, much less as to the mechanism whereby it takes place.

On page 19 the statement is made that "the new volcano (Parícutin) has remained in almost constant activity to the present day." This was certainly true at the time the manuscript of the book was prepared. Now, however, it has been completely inactive for more than a year (since March 4, 1952) and observations on numerous comparable volcanoes in the region make it appear extremely unlikely that Parícutin will become active again.

There are not many typographical errors in the book. The following should probably be mentioned: p. 18, par. 2, line 5 *unwelling* should read *upwelling*; p. 49, line 8 from bottom, *Fig. 1* should read *Fig. 2*; on p. 109 it is stated that "In the purest glass sands SiO_2 may exceed 90%—." SiO_2 must exceed 90% in any glass sand and in very pure ones used in optical glass the percentage must exceed 99.8%. This is probably a typographical error for 99%. P. 125, par. 3, line 9, *proportion* should read *portion*; p. 128, par. 4, line 6, *Plate 13B* should read *Plate 12B*.

As Shand so effectively points out in his historical introduction, chemists were particularly and chiefly interested in rocks and minerals until the middle of the 19th century. In the intervening 100 years, however, their attention has turned to investigations of synthetic organic and inorganic products, while that of geologists has focussed largely on stratigraphic and paleontologic problems. However, analytical chemical methods applicable to rocks and minerals as developed by Hillebrand toward the end of the 19th century, and work by other chemists, have convinced petrologists of the essential bond between chemistry and petrology. If this book can persuade the chemists that their original field of investigation, natural materials, still offers challenging problems, as I think it can, then it will have fulfilled its author's wish. Certainly the straightforward, lucid style of presentation will go a long way toward accomplishing this end.

EARL INGERSON

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SCHMUCK- UND EDELSTEINKUNDLICHES TASCHENBUCH, by KARL F. CHUDOBA AND EDUARD J. GÜBELIN, XII+158 pp., 2 colored plates, 25 illustrations and numerous tables in the text, and a supplement of 24 pages containing 124 half-tone cuts of mineral inclusions. Verlag Bonner Universitäts-Buchdruckerei, Gebrüder Scheur, G.M.B.H., Bonn, Germany, 1953. Price 19.60 marks.

Since World War II there has been greatly increased interest in Europe in ornamental and gem minerals, which has resulted in the publication of several books on gemology, the formation of several gemological associations, and the establishing of a specialized journal. The book by Chudoba and Gübelin is a recent addition.

Following a brief introduction, 32 pages are devoted to a glossary and the listing of approved names of gemstones and those commonly used in the trade. Terms used in the occurrence and cutting of gem minerals are discussed in 34 pages. Chemical and physical properties are sketchily described in Chapter 3 (33 pages). A rather comprehensive treatment of inclusions is given in Chapter 4 (24 pages), which is supplemented by 124 half-tone cuts. Then follow various summary tables and brief discussions of coated, synthetic, and imitation stones. There is also a very short chapter on the use of the microscope as applied to gemstones. Determinative tables make up the last chapter. There is no index.

The authors apparently aimed to have the book serve (1) as a dictionary and reference work and (2) to some extent as a text, which would appeal to jewelers and dealers in and

cutters and lovers of gemstones. Much valuable information has been compiled and arranged for ready reference. It is, however, doubtful that the book can be used successfully as a text, especially by beginners in gemology or by the general public, for the treatment is too sketchy and superficial. Moreover, even for one well versed in the German language the style is frequently very involved.

The book is well printed on good paper and bound with a flexible cover, but on account of its size, $5\frac{1}{2} \times 8\frac{1}{4}$ inches, it is not a "pocket" edition in the usual sense.

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THE MINERALOGY OF GREENLAND, by O. B. BØGGILD, pp. 422, 87 illustrations, and 1 map of Greenland, Vol. 149, No. 3, of *Meddelelser om Grønland*. C. A. Reitzels Forlag, Copenhagen, Denmark, 1953. Paper cover, price 65 kroner.

For more than 50 years Professor O. B. Bøggild has been an intensively active student of the minerals of Greenland. In 1905 he published "*Mineralogica Groenlandica*," 625 pages, as Vol. 32 of *Meddelelser om Grønland*. Since then many new mineral localities have been discovered. Moreover, during this period various scientific expeditions interested in the minerals of Greenland and the officers of mines and government stations collected quantities of minerals which were sent to Denmark for study. As a result, it was obvious that either a supplement to "*Mineralogica Groenlandica*" should be published or a new edition prepared. It is fortunate that it was decided to publish a new edition in English in order to make it more generally useful than the first edition which was in Danish. Less interesting occurrences were omitted and many descriptions of minerals and localities shortened. The various properties and the important occurrences of 251 minerals are described. In each case there is an exhaustive bibliography. The crystal drawings are excellent. There are also some very good half-tone cuts. There are alphabetical lists of localities and minerals. Dr. Bøggild indicates that 61 elements occur in the minerals of Greenland.

This volume, the result of an exhaustive and painstaking study, will long serve as a most valuable reference work on the mineralogy of Greenland.

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MEASUREMENT OF RADIO ISOTOPES, by DENIS TAYLOR, 118 pages, 40 diagrams, John Wiley and Sons, Inc., New York, 1951.

This highly useful small "pocket" book contains succinct descriptions of the various types of apparatus by means of which radioactivity may be detected and measured. Beginning with a chapter on fundamental theory, it continues with descriptions of radioactive measuring apparatus and counting systems, including D. C. ionization chambers, vibrating-reed electrometers, quartz-fiber electrometers, Geiger-Müller counters, beta-ray counters, gamma-ray counters, x-ray counters, flow-type proportional counters, and scintillation counters. Other chapters provide information on problems of source geometry, source absorption, dilution effects, source mountings and source standardizations. Also the author, who is head of the Electronics Division, Atomic Energy Research Establishment at Harwell, England, discusses in detail methods of measurement, correction factors, health hazards and the use of radiomonitors. The book is of considerable value to geologists and mineralogists who are interested in a general coverage of the field of radio isotope measurement and who do have neither the time nor inclination to search for such information in larger and more encyclopedic treatises on the subject.

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GEOLOGY OF THE CABALLO MOUNTAINS, by VINCENT C. KELLEY AND CASWELL SILVER, University of New Mexico Publications in Geology No. 4, 286 pages, 19 plates, 26 figures, 1952, \$2.50.

This publication on the general geology, stratigraphy and mineral deposits of the Caballo Mountains in central southern New Mexico continues the previously established high standard of the University of New Mexico Publications in Geology. The sequence of general subjects covered by the work is, introduction, stratigraphy (pre-Cambrian, Paleozoic, Cretaceous, Tertiary and Recent rocks all occur in the region), structure, physiography, ground water, and mineral deposits. Under the last heading are described a group of hypogene deposits, including those of lead, copper, fluorite and minor gold, silver and barite; supergene deposits of lead, copper, manganese; placer deposits of gold and manganese; and non-metallic mineral deposits including those of iron, limestone, dolomite, gypsum, clay and shale, sand and gravel, guano, as well as coal, oil and gas.

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REPORT OF THE COMMITTEE ON THE MEASUREMENT OF GEOLOGIC TIME, 1951-1952. Division of Geology and Geography, National Academy of Science-National Research Council, Publication 245, 151 pages, 1953, \$1.50.

This publication of the Committee on the Measurement of Geologic Time, which has appeared regularly since 1924, has gained in value with each new succeeding issue. The work of the late A. C. Lane and John P. Marble and their associates in attempting to bring under one cover a yearly condensation of the immense amount of work that is being carried on in many parts of the world on the methods and problems of measuring geologic time is a most necessary, difficult but deeply appreciated task. The Committee, of course, concerns itself not merely with radioactive age determination techniques, but also with many of the other less widely employed methods of geological chronology. The 1951-1952 report includes the following reports: (1) Summary report of the Committee by John P. Marble, Chairman. (2) Annotated bibliography of articles related to the measurement of geologic time compiled by John P. Marble. (3) Progress reports on work directed by various members of the Committee. (4) A translation from the Russian of an article by G. V. Voitkevich (*Acad. Nauk. S.S.S.R. Dokady n.s.*, 77(3), 461-464, 1951) entitled, Concerning the Age of the Earth. (5) Abstracts of a group of papers on radioactivity delivered at the 1952 meeting of the American Geophysical Union. (6) A note on the radioactive halo method by I. Hayase of Kyoto University, Japan. (7) A short summary of recent work on natural variations in stable isotopes by John P. Marble.

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